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Organic Analytical Reagents '

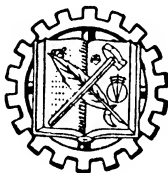
VOLUME ONE

BY

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TO MY FATHER

whose clear vision and deep understanding have contributed so much to the preparation of this work.

PREFACE

Since the earliest days of analytical chemistry, organic reagents have been employed in various ways to facilitate the detection and determination of chemical substances. Only during the past two or three decades, however, have these compounds been used extensively in analytical procedures. At present they are rapidly gaining in popularity because of their greater sensitivity and specificity as compared to inorganic reagents, and also because of the greater convenience with which they may be employed in many analytical procedures.

The principal purpose in preparing this book has been to assemble in one place a description of all organic compounds used in the analysis of inorganic substances, and to present a discussion of the methods employing these reagents.

The information used in this book is taken from all publications appearing prior to January 1, 1946. Due to conditions resulting from the war, foreign journals have been delayed or prevented from reaching the United States, and in consequence much of the material contained in the more recent publications has been taken from *Chemical Abstracts*. For this reason, not all articles published before January 1, 1946, have been reviewed. The chemist who uses this book in reviewing the literature may, however, be guided by this principle: that all articles appearing in *Chemical Abstracts* up to and including 1945, as well as all original journals available to this date, have been included.

References to the literature have been made so as to indicate, at least to some extent, the subject matter of each. Thus the chemist who wishes to use a certain reagent for a given purpose has available a comment on almost every article that has been written on the subject and, in addition, the reference to the original publication in the event he wishes to consult this source. In this connection, it may be helpful to note that bibliofilm or photostat copies of articles appearing in most chemical journals can be secured at moderate cost from the United States Department of Agriculture Library, Washington, D. C.

Many obviously inferior reagents and methods are included since the treatment of the subject is intended to be complete. The inclusion of inferior methods is justified because of two considerations: in the future no time need be lost in attempting analytical methods that in the past have been demonstrated as unsatisfactory; and further, an inferior method may, with suitable modifications, be made useful for certain purposes.

In order to promote a more comprehensive study and a wider use of organic compounds in inorganic analysis, methods have been included for the preparation of most compounds listed in the book. For most substances, several methods appear in the literature and, in selecting the one to be included, the author has been guided by the principle that it be the most adaptable in the average chemistry laboratory. It should be stated that only a few of the methods of synthesis described have been used by the author, and undoubtedly some may prove unsatisfactory. Consequently, any information regarding better methods is earnestly solicited.

The primary aim of this book has been to collect in one place all information relating to the analytical uses of a given compound, and this principle has been adhered to regardless of structural characteristics or analytical functions. In a classification based on functions alone, many compounds would necessarily appear in different sections. For example, benzidine is used as a reducing agent, a basic salinogenic compound and in diazotization and coupling reactions for nitrite. Further, any classifications based upon functional groups present in the organic molecule would be somewhat arbitrary, since many compounds possess more than one group which affects their chemical reactions. The plan finally adopted calls for the complete treatment of each compound in one section, since any disadvantage resulting from this lack of regard for function and structure is believed compensated by the convenience of localization of information. In general, chemically related compounds are grouped together in so far as this is practicable; thus, the alcohols, amines, acids, oximes, arsonic acids, etc., form separate sections. It must be emphasized that owing to the diverse character of the reagents used in analytical procedures the associations of these substances in separate sections of this book may be somewhat debatable from the purely chemical point of view, but the plan used here seemed to be the most practicable that could be devised by the author. Although this scheme may separate such substances as reducing agents or oxidizing agents through widely scattered parts of the book, every reference to a particular reagent will be found in the section devoted to that compound.

The author is painfully aware of the many inconsistencies and ambiguities which appear in various parts of this book. Contradictory claims made by various authors are purposely included in order that the analyst may properly evaluate their merit through additional research. Many vague descriptions of methods and procedures are presented simply because the original sources themselves are not clear. Frequently, too, in translations or in abstracts errors have been discovered, which indicates too clearly that many more must certainly have escaped notice. The possibility of any error, or incompleteness of description has not prevented inclusion of certain important material, since such omissions would lead to incomplete coverage of some topics. The author also realizes that he must accept the responsibility for many mistakes, and he earnestly hopes that these will be communicated to him.

Another source of error has appeared in many publications: due to the character of chemical nomenclature, often there has been some doubt as to exactly what compound is referred to in certain discussions. This is especially true of the dyes, but is true also of certain other compounds. Every effort has been made to see that these references have been properly evaluated.

Indianapolis, Ind.
August, 1946

F. J. W.

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Dr. G. Frederick Smith of the University of Illinois and Dr. Harvey Diehl of Iowa State College have kindly supplied the author with the material for the synthesis of cyclohexandionedioxime.

The author further wishes to express his thanks to the American Chemical Society for permission to reproduce a number of procedures and tables taken from the *Journal of Industrial and Engineering Chemistry, Analytical Edition*, and from the *Journal of the American Chemical Society*; to the J. T. Baker

Chemical Company for permission to use a table taken from the *Chemist-Analyst*, and to the G. Frederick Smith Chemical Company for permission to use much valuable information taken from booklets on the dioximes and phenanthrolines published by this company.

And finally, no thanks can adequately repay the patient self-denial of his wife and sons, who have spent altogether too many months without the companionship and associations which in normal times they have so much enjoyed.

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INTRODUCTION

ORGANIC compounds serve in a variety of ways to simplify and facilitate procedures in inorganic analysis. The most common applications are as wash liquids and solvents, oxidizing agents, reducing agents, indicators, primary standards in acidimetry and alkalimetry, as acidic and basic salt-forming compounds, photometric aids and for control of adsorption, and as diazotization and coupling agents for the detection and determination of nitrites. Thus it will be seen that, from the almost limitless number of possible organic compounds, many may be found which will definitely be superior for a given purpose as compared with inorganic substances, which are limited in number.

Water is the only inorganic solvent which can be employed conveniently in analytical procedures. Consequently, as long as water alone is used, separations and color reactions useful in analysis are limited to those which can be successfully carried out in an aqueous medium. With the use of organic liquids, however, a wide variety of solvents consisting of alcohols, ethers, esters, aldehydes, and ketones, as well as mixtures of these with one another or with water, may be used. By the proper use of organic liquids many useful but otherwise difficult analytical procedures may be carried out. For example, with the use of organic liquids the chemist is able to effect separations which otherwise would be difficult or impossible. Further, the solubility of certain salts is decreased by the addition of such liquids as ethyl alcohol and acetone to their aqueous solutions. This makes possible the complete precipitation of these substances which are not sufficiently insoluble in pure water to make their separation quantitative. Typical of this type of procedure is the addition of ethyl alcohol to an aqueous solution of a lead or calcium salt to make possible the complete precipitation of lead or calcium as the sulfate.

When acetone is added to the aqueous solution in the test for cobalt or iron by the thiocyanate method, the sensitivity of the color reaction may be increased greatly. This is caused by the change in the activities of ions upon the addition of organic liquids.

By the use of organic liquids which are immiscible with water, it is possible to extract and concentrate many compounds which are more soluble in the organic solvent than in water. In this way the sensitivity of many tests may be increased. This is illustrated by the addition of ether in the test for chromium, which is based on the conversion of chromium to perchromic acid, or by the use of carbon tetrachloride or carbon disulfide in testing for free iodine or bromine. Many separations which would be difficult with inorganic reagents are easily effected by extracting salts of the metals and organic reagents from aqueous solutions with immiscible liquids. Chloroform and carbon tetrachloride, for example, are used to extract the dithizonates of metals from aqueous solutions at different acidities.

The number of inorganic acids and bases which may be used for neutralizations and for the adjustment of pH in aqueous solutions is rather limited, being confined to ammonium hydroxide, the alkali hydroxides and the mineral acids. With the exception of a few such as ammonium hydroxide, boric acid and phosphoric acid, these substances are strong electrolytes, making a delicate control of acidity or alkalinity difficult when they are employed. Organic acids and bases, which exhibit a wide variation in their degree of ionization, are very useful for the control of pH of aqueous solutions. Organic acids and bases and their salts are commonly used as standards in analysis and in the preparation of buffer solutions. Further, many organic acids are used to form salts, such as in the precipitation of calcium oxalate with oxalic acid or ammonium oxalate, and also for the formation of complex ions or molecules. This latter application is particularly important in the elimination of interference in analytical procedures, or for the separation of various ions. The acids most frequently used for this purpose are oxalic, citric and tartaric acids.

The number of organic reagents which have been used as oxidizing reagents in analytical chemistry is rather limited, but some of these, such as chloramine and methylene blue, are extremely useful. These compounds may be used in the preparation of standard oxidizing solutions.

Reducing agents have numerous applications in analytical chemistry. The number of inorganic reducing agents is limited, but the number of organic compounds used for this purpose is very large. For example, molybdenum, phosphorus and silicon may be determined colorimetrically after reducing the complex phospho- and silicomolybdates to the blue reduction products with hydroquinone, phenylhydrazine or 1,2,4-aminonaphtholsulfonic acid; and metals like silver and gold may be determined colorimetrically after reduction to colored colloidal suspensions by such reducing agents as dextrin, formaldehyde and glucose. Some cations such as gold and palladium may be reduced to the free metal by the action of reducing agents such as hydroquinone, acetylene or ethylene, and then determined gravimetrically.

Many organic reducing agents are converted by inorganic substances to colored oxidation products which may be measured for the indirect determination of the oxidizing agent, or observed for the detection of the inorganic ion. Thus, benzidine and o-tolidine are converted to blue oxidation products by the action of oxidizing agents such as manganese dioxide and lead dioxide.

Many organic acids and bases undergo a molecular rearrangement with change in color when treated with a base or acid and these compounds are extremely valuable as hydrogen ion indicators. Some organic oxidizing and reducing agents may be used as oxidation-reduction indicators. If the two forms of a compound have different colors, the indicator may be used reversibly. Many organic compounds such as eosin, bromophenol blue and fluorescein may be used as adsorption indicators for the titration of silver and halides. Because of the vast amount of material relating to the theory and use of indicators, a discussion of this subject has not been undertaken in this book.

Many organic compounds possess reactive groups which enable them to form ring structures containing a metal atom. These products are known as chelate compounds or inner-complex salts. Since these compounds are generally

characterized by their low solubility in water, and by the additional fact that in many instances they are highly colored, they are of unusual importance in their analytical applications. Structures which are capable of forming inner-complex salts with metals are frequently specific or highly selective in their action, and consequently offer attractive possibilities as analytical reagents. Because of the importance of this subject, it will be treated in some detail in the following chapters.

Some organic compounds owe their analytical usefulness to the fact that through reactions involving inorganic substances they are converted into different organic compounds with consequent distinctive changes in properties. Among the examples of this type of procedure is the detection of bromide through conversion of fluorescein to eosin; the formation of methylene blue in the reaction between p-aminodimethylaniline and hydrogen sulfide; and the detection of nitrate by the conversion of certain aromatic compounds to the corresponding nitro derivatives.

Finally, some organic compounds, such as gelatin, gum arabic, gum acacia, starch, egg albumin, etc., are used to prevent or at least decrease the rate of coagulation and precipitation of finely divided suspensions such that they may be used in colorimetric procedures.

CHAPTER I

THE ELECTRONIC THEORY OF VALENCE

THE early study of the structure of molecules was based on methods which were principally chemical in character, and this later was supplemented by various physical methods, including the study of crystal structure by diffraction of x-rays and of gas molecules by the diffraction of electron waves, the measurement of electric and magnetic dipole moments, the interpretation of band spectra and Raman effect and the determination of entropy values. From these sources a great amount of information has been obtained regarding the atomic configuration of molecules and crystals, and also the distribution of electrons within atoms and crystals.

Originally the valence bond was represented by a line drawn between the symbols of 2 chemical elements, but while this symbolism expressed many chemical facts it conveyed no information whatsoever regarding the nature of the bond which joined the atoms in the molecule. This was completely unknown.

Following the discovery of the electron and the development of the structure of the atom by Rutherford and Bohr, numerous attempts were made to explain compound formation on the basis of electron distribution within the atoms of the reacting elements. In 1916 G. N. Lewis¹ published a paper in which an electron theory of the chemical bond was proposed, and this serves as the basis for the modern electronic theory of valence. Langmuir² further applied the new concept of valence to the coordination and clarification of the many facts of chemical behavior.

The electronic theory of valence is based on three fundamental principles, which are stated briefly as follows:

1. Compound formation is caused by the tendency of the electrons external to the nuclei of atoms to undergo rearrangement so as to form the most stable possible groupings. In general, the most stable groups are those corresponding to the inert gases. In the helium atom there are 2 electrons in the outer level, and in all other inert gases there are 8. Certain other stable groups are known, but these occur less frequently than the inert gas structures.

2. A stable grouping may be attained by the complete transfer of one or more electrons from one atom to another.

3. A stable grouping may also be attained by the sharing of pairs of electrons between 2 atoms.

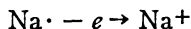
A chemical bond exists between 2 atoms or groups of atoms if the forces between them are such as to lead to the formation of an aggregate of sufficient stability to be regarded as an independent molecular species. Chemical and physical evidence indicates that such bonds are formed under different circumstances and impart to the molecules which result from their formation different properties and different degrees of stability. In order to understand better the

nature of chemical compounds it is necessary to be familiar with the different types of chemical bonds and their characteristics.

For convenience chemical bonds are classified into three extreme types: electrostatic bonds, covalent bonds and metallic bonds. It must be emphasized, however, that although bonds of each type possess well-defined properties, the transition from one extreme type to another may be gradual, and thus permit the existence of bonds of intermediate type. The nature of the different types of bonds is discussed in the following sections.

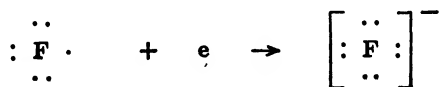
Ionic bonds. An electrostatic bond is formed when each of 2 atoms or groups of atoms attain an electronic structure, essentially independent of the presence of the other atom or group, such that electrostatic forces are developed which are of sufficient strength to form a chemical bond. The most important of the electrostatic bonds is the *ionic bond*. Such bonds result from the transfer of one or more electrons from one atom to another whereby two oppositely charged ions are formed, and these ions are held together only by non-directed electrostatic forces.

The atoms of metallic elements lose their outer electrons easily, whereas atoms of non-metallic elements tend to acquire additional electrons to form stable cations and anions, respectively. Each ion forms a complete atomic core in which the group of extra-nuclear electrons has the same configuration as that of the nearest inert gas in the periodic system, and this structure is essentially retained as the ions approach one another to form a stable molecule or crystal. For example, the sodium atom has a nuclear charge of +11, and about the nucleus are grouped 11 negatively charged electrons; hence, the sodium atom is electrically neutral. The neutral fluorine atom has a nuclear charge of +9 and 9 electrons are grouped about the nucleus. If a sodium atom and a fluorine atom are brought relatively close together in space the sodium atom loses the 1 electron in its outer level and thereby acquires a structure similar to that of the stable neon atom. However, the sodium atom, having lost 1 electron, now is no longer electrically neutral, but has a net charge of +1. It thus becomes a univalent positive ion.



In this and similar expressions the Lewis electronic formulas are used in which the symbol of the element represents the *kernel* of the atom, consisting of the nucleus and all electrons except those in the outer or valence shell; these are shown by dots grouped about the symbol.

When the fluorine atom acquires 1 electron it assumes the configuration of the stable neon atom, and has a charge of -1; it thus becomes a univalent negative ion.



When associated in the solid state there are no discrete sodium fluoride molecules, but instead the crystal is composed of sodium cations (Na^+) and fluorine

anions (F^-), each of which is strongly attracted to and held by 6 oppositely charged ions which surround it octahedrally. Thus the ionic bonds join all ions into one giant molecule. When the solid is dissolved in some solvent of high dielectric constant, such as water, the mutual attraction of the oppositely charged ions is sufficiently reduced causing them to separate and lead virtually independent existences. If the solid is vaporized the sodium and fluoride ions form closely associated ion pairs.

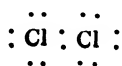
In complexes such as $[Fe(H_2O)_6]^{+++}$ and $[Ni(H_2O)_4]^{++}$ the bonds between the central atom and the surrounding molecules are caused by the electrostatic attraction of the charged central atom for the permanent electric dipoles of the molecules. Bonds of this type are called *ion-dipole* bonds.

Electrostatic bonds may also result from the attraction of an ion for the induced dipole of a polarizable molecule, or for the mutual attraction of permanent electric dipoles of 2 molecules.

Covalent bonds. In the molecules of hydrogen, methane, carbon tetrachloride and many other compounds, a transfer of electrons from one atom to another does not occur. Evidence indicates, however, that even in molecules of this kind each atom attains the electron grouping of a neighboring inert gaseous element, or that of some other stable configuration. This stability results from the sharing of electrons by 2 atoms. Each atom shares its own electron or electrons with the other. If each of 2 atoms shares 1 electron with the other, a union of the 2 atoms occurs through the mutual attraction of their positively charged nuclei for the pair of electrons. Thus, bond formation is effected without either atom acquiring an electrical charge. This type of linkage is called *covalence*. In the hydrogen molecule each of 2 hydrogen atoms shares its 1 electron with the other with the result that each atom assumes the configuration of the stable helium atom



Two chlorine atoms share 1 electron each so that each atom is surrounded by 8 electrons in its outer level, thus corresponding to the stable argon configuration.

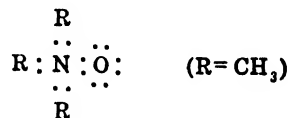


Thus it will be seen that a pair of electrons held jointly by 2 atoms is effective in completing a stable electron group for each.

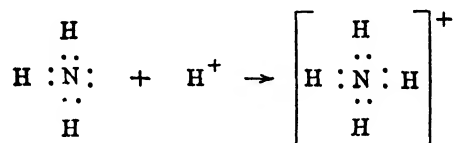
Each pair of shared electrons constitutes a single valence bond. This is conventionally represented by organic chemists by the single dash. Double and triple bonds are formed by the sharing of 4 and 6 electrons, respectively. These bonds are represented by the double and triple bond symbols of organic compounds as in the following examples.



The normal covalent bond described above consists of mutually shared electrons. In some examples of covalent bond formation, however, both electrons of the shared pair originally belonged to 1 atom. Lewis has assigned to trimethylamine oxide the following electronic formula



in which it will be observed that the nitrogen atom possesses the stable neon structure with a completed octet of valence electrons. The nitrogen atom thus forms 4 single covalent bonds and the oxygen atom 1. Assuming the shared pair of electrons to be divided between the 2 atoms which they join, the nitrogen atom is found to possess 6 extra-nuclear electrons, whereas the nuclear charge is +7. The nitrogen atom thus has an electrical charge of +1. Similarly, the oxygen atom is found to have 9 electrons and a nuclear charge of +8; this gives the atom an electrical charge of -1. These charges are generally called *formal charges*, and do not show the general or actual distribution of electrical charges among the atoms of a molecule or complex ion. Thus, for example, in the ammonium ion, which is formed by the linking of a proton to an ammonia molecule through the unshared pair of electrons of the nitrogen atom,



the positive formal charge of the nitrogen atom is not to be regarded as belonging exclusively to the nitrogen atom, but rather a part of the excess positive charge can be considered to be transferred to each of the hydrogen atoms.

From a consideration of the formal charges of the nitrogen and oxygen atoms in trimethylamine oxide, plus the fact that these atoms are covalently linked, the bond between them may be regarded as a type of double bond composed of 1 single covalent bond and 1 ionic bond of unit strength. Such linkage has variously been called a *dative bond*, a *semi-polar bond* or a *coordinated covalence bond*. The coordinate link is usually represented by an arrow (\rightarrow) to show the direction of electron donation. The atom providing both electrons is referred to as the *donor* atom, and the one receiving them as the *acceptor* atom.

In representing normal and coordinate covalence bonds in chemical compounds by conventional symbols, it is not implied that a difference necessarily exists in the nature of the bond once it is formed, but the distinction in the manner of its formation is often useful in the study of chemical compounds.

The metallic bond. Since the metallic bond is of little significance in the chemistry of organic analytical reagents, this type of linkage will be discussed only briefly here. Lorentz³ has proposed a theory of metals which is useful in explaining qualitatively many of their characteristic properties. This

theory has recently been developed by an application of quantum mechanics. According to Lorentz a metal is a crystalline arrangement of metal cations with free electrons moving in the spaces between them. This free-electron theory accounts satisfactorily for such metallic properties as luster and other optical properties, high electrical and thermal conductivity, and high heat capacity.

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2. I. Langmuir, *J. Am. Chem. Soc.*, **41**, 868, 1543 (1919).
3. H. A. Lorentz, *The Theory of Electrons*, Teubner, 1916.
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CHAPTER II

COORDINATION COMPOUNDS

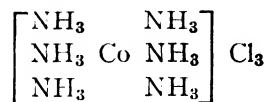
MANY compounds are known which are formed by the union in stoichiometric ratio of otherwise saturated molecules which are themselves capable of independent existences. Typical of such compounds are the ammines of trivalent cobalt, the numerous complex cyanides and the alums. As an illustration of the formation of such substances it may be noted that one molecule of ferrous cyanide can combine with 4 molecules of potassium cyanide to form stable potassium ferrocyanide $K_4Fe(CN)_6$, which has properties that are entirely different from those of either of the constituent compounds, and which in aqueous solution dissociates into potassium and ferrocyanide ions. Such compounds were formerly called *molecular compounds*, but were later termed *coordination compounds* by Werner. Such substances are very numerous and are of fundamental importance in analytical chemistry, as well as in inorganic and organic chemistry.

The Werner theory. Attempts to formulate coordination compounds on the basis of the classical valence theory fail completely if the usual valences of atoms in compounds are retained. It must be assumed that apparently saturated compounds still possess additional combining capacity by virtue of which coordination compounds are formed. In order to explain this fact, Alfred Werner¹ in 1891 introduced the concept of auxiliary or secondary valence. According to Werner, without invoking the aid of any special valence theory, neutral molecules or oppositely charged ions are grouped or *coordinated* about a central ion in what he termed the *first sphere of attraction* or *coordination sphere*. The number of such groups which may be arranged about the central ion is the *coordination number*, and this is a characteristic property of that ion. As a general rule the coordination number is 2, 3, 4, 6 or 8, or values which allow spatially symmetrical arrangements of the attached groups. For the majority of metals this number is 6, and in some cases 4, and for the non-metals such as sulfur, phosphorus, carbon, nitrogen and boron it is 4. Complexes are known, however, in which the coordination number is 2 and in others 8.

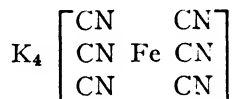
The coordination number is independent of the nature of the group attached to the central atom. Thus, neutral water molecules, chloride, bromide, iodide, cyanide and hydroxyl radicals, oxygen atoms and ammonia molecules occupy only 1 coordination position each. On the other hand, bivalent radicals such as oxalate, sulfate and carbonate may occupy 1 or 2 coordination positions.

In general, the tendency to form the central atom of a coordination complex decreases with increasing potential. This is illustrated by the fact that comparatively few complexes containing the alkali metals are known, whereas most of the compounds of the noble metals, which lie at the bottom of the electrochemical series, are complex in character.

According to the Werner concept, in hexammine cobaltic chloride six ammonia molecules are coordinated about the cobaltic ion to form a new and complex ion $[\text{Co}(\text{NH}_3)_6]^+$. The chlorine is bound in the "second sphere of attraction," or, according to modern expression, exists as an independent anion. The compound is represented in the following manner



Similarly, potassium ferrocyanide is formulated as



in which the cyanide groups are arranged octahedrally about the central iron atom, and bound to it by auxiliary valences which are equivalent to each other.

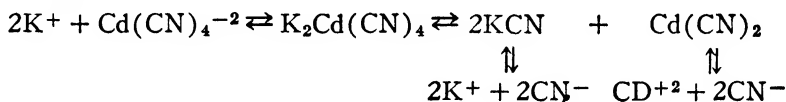
The Werner system of writing formulas for complex compounds has been of inestimable value for two reasons: (a) with its aid the steric structure of the solid compound is clearly and accurately shown; and (b) the behavior of these compounds in aqueous solution is indicated. Thus, the foregoing formula shows that potassium ferrocyanide dissociates into 1 ferrocyanide and 4 potassium ions, and that the bond between the iron and cyanide ions is complex and that few if any ferrous or cyanide ions are present in solution.

Before proceeding further with a discussion of coordination compounds, it is important to define more rigorously the conception of such substances. The qualifying principle generally employed is that the compound persists as a coordination complex in solution. This definition is made necessary by the fact that many compounds are known which superficially appear to be coordination complexes, but which differ in certain important respects from those compounds definitely established as belonging to this class. For example, the study of crystals reveals that certain crystal lattices may contain units which are not chemically combined, but which, by crystallizing together in stoichiometric ratio, form a new lattice. When this crystal dissolves in water, however, the units separate and exist independently of each other; the combination ceases to exist. Such combinations are known as *lattice compounds*. Belonging to this class of substances are many compounds which can be formulated only with difficulty in terms of the Werner theory, or which involve coordination numbers of 5 and 7. For example, cesium chloride, CsCl , forms with cobaltous chloride, CoCl_2 , a double salt corresponding in composition to Cs_3CoCl_5 . In this compound cobalt appears to have a coordination number of 5, a value unknown except in a few cases. It is known, however, that in the crystal lattice both CoCl_4^{-2} and Cl^- anions exist independently, and that in solution there is no evidence whatever of the CoCl_5^{-3} anion. Thus, the compound appears to be a lattice compound composed of $\text{Cs}_2\text{CoCl}_4 + \text{CsCl}$, which exists only in the solid phase.

Similarly, in $(\text{NH}_4)_3\text{ZrF}_7$ the zirconium atom does not have a coordination number of 7, since the compound is actually represented as $(\text{NH}_4)_2[\text{ZrF}_6] + \text{NH}_4\text{F}$. Alums and other double salts also belong to this class of compounds.

A comparison of the properties of brown cesium rhodium alum $\text{CsRh}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and the red double sulfate $\text{Cs}[\text{Rh}(\text{SO}_4)_2] \cdot 4\text{H}_2\text{O}$ serves to illustrate the difference between coordination compounds and lattice compounds. The existence of the true complex anion $[\text{Rh}(\text{SO}_4)_2]^-$ in the double sulfate is indicated by the fact that its solution yields no immediate precipitate with barium chloride, while the alum gives all the reactions of the sulfate radical.

Classification of coordination compounds. A study of the properties of coordination compounds reveals that these substances may be classified into two limiting types. Many compounds, such as the amines of metallic salts, dissociate reversibly into their components either in solution or in the solid phase. This indicates that the components are not firmly bound. Many complex anions are similarly dissociated. This is illustrated by the dissociation of $\text{K}_2\text{Cd}(\text{CN})_4$.



Compounds of this type have been called *normal complexes* by Biltz.² On the other hand, many complexes, such as the ferrocyanide anion or the hexammine cobaltic cation do not dissociate reversibly, and the coordination linkage exhibits the same strength and directional properties as a normal covalent bond. These compounds are termed *penetration complexes* by Biltz.

Basis of the Werner theory. A brief review of some of the evidence offered in support of the Werner theory will prove helpful in understanding the character of coordination compounds. By various methods 7 hexammine salts of platinum are formed by the successive replacement of from 1 to 6 molecules of ammonia by chlorine. These compounds are shown in Table 1.

TABLE 1.

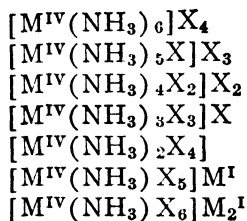
No.	Formula	Complex Ion	Molar Conductivity at 1000 l. Dilution 25° C.
I	$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	Tetravalent cation	523
II	$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$	Trivalent cation	404
III	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$	Divalent cation	228
IV	$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	Monovalent cation	97
V	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	Neutral	0
VI	$[\text{Pt}(\text{NH}_3)\text{Cl}_5]\text{K}$	Monovalent anion	109
VII	$[\text{PtCl}_6]\text{K}_2$	Divalent anion	256

If compound I is treated with silver nitrate, all chlorine is precipitated thereby indicating that all chlorine atoms exist independently as chloride ions. This fact

is further supported by data obtained by measuring the electrical conductivity of solutions of the compound. The molar conductivities of all salts of the same valence type are approximately the same, whereas corresponding values for salts of different valence types are distinctly different. For example, at a dilution of 1000 liters and at a temperature of 25° C., binary electrolytes such as sodium chloride and potassium chloride have a molar conductivity of approximately 125. For ternary electrolytes, such as magnesium chloride and calcium chloride, this value is about 250, and for quaternary electrolytes, such as aluminum chloride and ferric chloride, the molar conductivity is about 425.

The molar conductivity of compound I (Table 1) at a dilution of 1000 liters and at 25° C. is 523, which indicates unmistakably that it dissociates into 5 ions. Similarly, silver nitrate precipitates only three fourths of the chlorine in compound II, and conductivity measurements indicate that it dissociates into 4 ions. In compound II, then, one of the chlorine atoms appears to be bound covalently to the central platinum atom as a part of the coordination complex. This fact is indicated by a special symbol introduced by Werner; the square bracket is used to enclose the atoms which form the coordination complex and which are not ionized. This symbol is an essential part of the Werner theory, and its position is indicated in the formula of a compound only after the degree and nature of ionization have been experimentally determined. The character of the remaining platinum ammine salts is interpreted in a manner similar to that employed for the first two. In all these compounds the coordination number is 6.

Many compounds similar to the hexammine platinum salts are known. For tetravalent metals having a coordination number of 6, these compounds may be represented by the following general formulas:



The acid radicals, designated by X in the foregoing formulas, usually found in complex compounds are chloride, bromide, iodide, cyanide, thiocyanate, nitrite, nitrate, sulfite, sulfate, carbonate and oxalate.

Reference to these general formulas shows that whenever a molecule of ammonia is replaced within the complex by a monovalent acid group, such as the chloride ion, the complex loses 1 positive charge, and its electrovalency decreases by 1 if it is positive and increases by 1 if negative. This characteristic change in electrovalence is universal in all such series of compounds, regardless of whether the central atom is platinum, cobalt, chromium or some other metal, or whether the neutral molecule is ammonia, water or some other group. The same is true irrespective of the value of the coordination number of the central atom. Platinous chloride, for example, yields a series of amines similar to

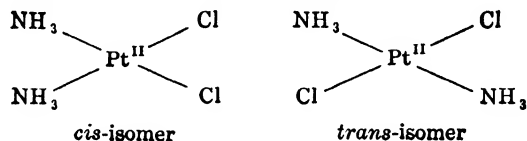
those with platonic chloride, but in this case the coordination number is 4. These compounds are shown in Table 2.

TABLE 2.

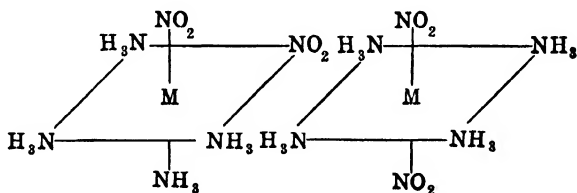
Formula	Complex Ion	Molar Conductivity at 1000 l. Dilution 25° C.
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	Divalent cation	260
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$	Monovalent cation	116
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	Neutral	0
$[\text{Pt}(\text{NH}_3)\text{Cl}_3]\text{K}$	Monovalent anion	107
$[\text{PtCl}_4]\text{K}_2$	Divalent anion	267

The same relationships are recognized in this series as in that of the platonic compounds.

Stereochemical considerations. It has been noted that the Werner theory is based essentially on stereochemical considerations. Thus, Werner assigned definite positions in space to the groups in a coordination complex. Van't Hoff had already established that when 4 groups are arranged about a carbon atom, they are directed toward the corners of a regular tetrahedron, but for the 4-coordination compounds of platinum a similar distribution was considered impossible, since these compounds are never optically active. Compounds of the type PtA_2B_2 , however, occur in 2 geometrically isomeric forms. This is explained if we assume that the 4 groups are located in the same plane with the central atom, but not if they occupy the corners of a tetrahedron. This is understood by reference to the following figure



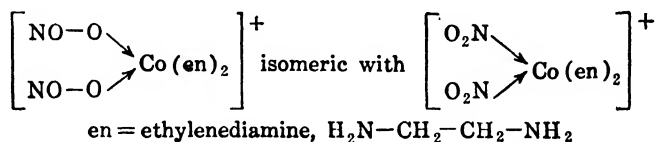
Werner assigned to the groups in a 6-coordination complex the simplest three-dimensional distribution, which is represented by the corners of a regular octahedron. This he justified by demonstrating that certain compounds, which on the basis of this assumption would be composed of asymmetric molecules, could in fact be resolved into optically active forms. Further, in certain 6-coordination compounds, 2 geometrical isomers are possible if we accept the octahedral concept of spatial distribution.



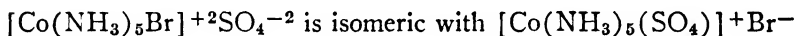
Only 2 isomers corresponding to the foregoing compounds are known, which is in agreement with Werner's prediction, and this view is further strengthened by the fact that since only 2 isomers are known, the 6 groups could not be distributed at the corners of a plane hexagon or of a trigonal prism, in which cases 3 isomers would be possible.

Isomerism of complex compounds. Seven types of isomerism are predicted by Werner's coordination theory. Optical and geometrical isomerism have been discussed in the preceding section. The remaining five types with examples are:¹⁵

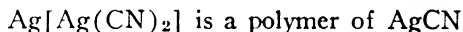
1. Structural isomerism:



2. Ionization isomerism.



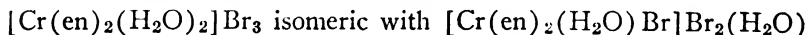
3. Coordination polymerism.



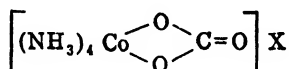
4. Coordination isomerism.



5. Hydration isomerism.

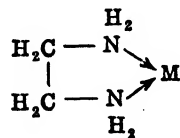


Cyclic compounds formed by coordination. A number of divalent anions are capable of occupying two positions in the coordination sphere surrounding a metal atom. Among the radicals which are found in such complexes are sulfate, sulfite, thiosulfate, selenate, selenite, chromate and molybdate. Four-membered rings are formed when these groups coordinate, and as a rule only one such group occurs in a single molecule. This type of coordination compound is illustrated by the following structure.



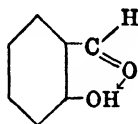
In a few instances compounds are known in which 3 rings are formed as a consequence of coordination by bifunctional groups alone. This is true in $[\text{Co}(\text{SO}_3)_3]\text{Na}$ and $[\text{Fe}(\text{SO}_4)_3]\text{Na}_3$.

Other bifunctional groups such as ethylenediamine also give rise to cyclic structures through the coordination of each of the 2 amine groups about a central atom. These compounds are represented by the following formula.



Cyclic structures of this type have been termed *chelate rings* by Morgan.³ The term chelate is derived from the Greek word $\chi\eta\lambda\eta'$, which means *claw*, and refers to the claw of the lobster and other crustaceans to which the chelate attachment may be imagined to bear some resemblance.

Originally the term chelate was used to designate those cyclic structures which result from the union of metallic atoms with organic and inorganic molecules. Later, however, the concept of chelation was extended to include such organic structures as those formed by the coordination of a hydrogen atom to the oxygen atom of an adjacent carbonyl group in the same molecule as in salicylaldehyde,



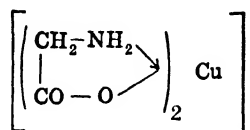
or in the coordination between two molecules as in the dimers of the carboxylic acids. In general, however, the chelate compounds containing a metallic atom are of the greatest analytical importance.

Many compounds such as $[\text{Co}(\text{NH}_3)(\text{NO}_2)_3]$ which contain equal numbers of neutral groups and monovalent anions coordinated about a metal atom are non-electrolytes. If the neutral group and acid radical are combined as a part of the same molecule the resulting coordination compound formed is in many cases very stable, very slightly soluble in water, but quite soluble in organic solvents. Non-electrolytes of this type have been called *inner-complex* salts by Ley.⁴ These complexes are very unusual in that they are extremely insoluble in water, but are generally soluble in non-polar solvents. They are usually characterized by very striking colors which differ markedly from the colors of the normal salts of the metals. Further, they are generally very stable.

Reference to the older literature reveals numerous instances where the terms inner-complex and chelate compounds are confused. This may be serious since not all chelate compounds possess the unusual characteristics associated with inner-complex salts. Consequently, the term *inner-complex* is reserved specifically for chelate non-electrolytes.

Aminoacetic acid, $\text{H}_2\text{N}-\text{CH}_2-\text{CO}_2\text{H}$, is typical of the compounds containing groups capable of forming inner-complex salts. Through the salt-forming character of the carboxyl group and the coordinating nitrogen atom of the amine

group, aminoacetic acid yields with such metals as copper and cobalt inner-complexes of the type



The cobalt compound exists in two isomeric forms. These are remarkably stable, and may be dissolved in concentrated sulfuric acid without change. Their aqueous solutions are practically non-conducting. The copper salt, in contrast to copper acetate, does not add ammonia, and its aqueous solution has a low electrical conductivity. Further, the deepening of the color, and the fact that no precipitation occurs on the addition of bases indicates that the copper compound is not a normal salt.

The great analytical usefulness of the inner-complex compounds lies in the fact that certain atomic groupings may confer the property of forming inner-complex salts more or less specifically with a certain metal. This means that the complex formed with that metal is usually distinguished from all others by a characteristic color, and also in most instances by low water solubility. Thus, from the enormous number of organic compounds containing suitable chelating structures it appears likely that future research will reveal many which are capable of specific action. Because of the great analytical importance of chelate compounds, a more detailed discussion of these compounds will be presented in the next chapter.

Stabilization of valency states by complex formation. It is an interesting fact of considerable analytical importance that oxidation-reduction potentials of systems may be profoundly affected by the attachment to an atom of strongly coordinating groups. This often leads to the stabilization of a valency state such that stable coordination compounds are known although normal derivatives are unstable. For example, cobalt may be oxidized electrolytically to the trivalent state, but the corresponding sulfate and alums are very unstable and tend to revert to the bivalent state. In the presence of ammonia, however, $[\text{Co}(\text{NH}_3)_6]^{+2}$ is oxidized to $[\text{Co}(\text{NH}_3)_6]^{+3}$ by atmospheric oxygen at room temperature.

Both cupric and cuprous ions are stabilized by suitable coordinating groups. The instability of cupric iodide is well known, but $[\text{Cu}(\text{en})_2]\text{I}_2 \cdot \text{H}_2\text{O}$, (en = ethylenediamine), is stable and shows no tendency to change to the cuprous state.⁵ The coordination of thiourea or ethylenethiourea similarly stabilizes the cuprous state so that salts of complex cuprous ions may be formed. Typical of these are $\{\text{Cu}[\text{CS}(\text{NH}_2)_2]_2\} \text{NO}_3$ and $\{\text{Cu}[\text{CS}(\text{NH}-\text{CH}_2)_2]_4\} \text{NO}_3$.

By the oxidation of silver nitrate with persulfate in the presence of pyridine a compound corresponding to $[\text{Ag}(\text{py})_4]\text{S}_2\text{O}_8$ is formed. Complex argentate cations containing o-phenanthroline⁶ and dipyriddy⁷ are very stable and many of their salts have been prepared. The argentate cation containing dipyriddy corresponds to $[\text{Ag}(\text{dipy})_2]^{+2}$, in which dipy = dipyriddy.

Of particular analytical interest is the stabilization of ferrous ions by coordination with dipyriddy and o-phenanthroline. Normal ferrous salts are readily oxidized by atmospheric oxygen, whereas salts of the type $[\text{Fe}(\text{phth})_3]\text{X}_2$ and $[\text{Fe}(\text{dipy})_3]\text{X}_2$ are more stable than the ferric compounds.^{8,9,10,11} It is interesting to note in this connection that the chelating compounds α -pyridylhydrazine¹² and α -pyridylpyrrole¹³ are said to favor the stability of the ferric state. β -Diketones behave similarly.

Diketones which normally form only mono-enol salts such as $\text{CH}_3-(\text{OTI})=\text{CH}-\text{CO}-\text{CH}_3$ yield dienolates through the formation of complex salts with carbon disulfide.

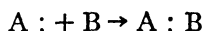
The foregoing examples illustrates the remarkable selective action of coordinating groups, and indicate one of the reasons why organic compounds in the future may be expected to play an increasingly important role in inorganic analysis.

The effect of coordination on oxidation-reduction potentials is shown in Table 3.

TABLE 3. OXIDATION-REDUCTION POTENTIALS

Equilibrium	Oxidation-Reduction Potential (volts)
$\text{Co}^{+2}/\text{Co}^{+3}$	+1.8
$[\text{Co}(\text{CN})_6]^{-4}/[\text{Co}(\text{CN})_6]^{-3}$	-0.8
$\text{Fe}^{+2}/\text{Fe}^{+3}$	+0.74
$[\text{Fe}(\text{CN})_6]^{-4}/[\text{Fe}(\text{CN})_6]^{-3}$	+0.49
$[\text{Fe}(\text{phth})_3]^{+2}/[\text{Fe}(\text{phth})_3]^{+3}$	+1.14
$[\text{Fe}(\text{dipy})_3]^{+2}/[\text{Fe}(\text{dipy})_3]^{+3}$	+1.1 (approx.)
$[\text{Fe}(\text{nitro-phth})_3]^{+2}/[\text{Fe}(\text{nitro-phth})_3]^{+3}$	+1.25

Theories of coordinate linkage. In order to explain the formation of coordination complexes, Sidgwick¹⁴ advanced the theory that the bond between the coordinate group and the central atom is a special covalency in which both electrons are supplied by the same atom. The characteristic common to all molecules or ions capable of being coordinated to metal atoms is the possession of at least one "lone pair" of electrons. Further, it has been found that the number of coordinate bonds which may be formed by one coordinate group is never greater than the number of "lone pairs" available. Thus, according to Sidgwick the coordinate link is simply a special case of the semi-polar type of bond (dative bond) in which the coordinate group acts as the donor and the central atom as the acceptor. When a coordinate link is formed between 2 atoms, 1 atom contributes to the other a share of its own previously unshared electrons. This is shown by the following equation:

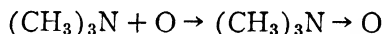


Thus it will be seen that, unlike in normal covalence, 2 atoms of different character are required for the formation of the coordinate link. According to this

concept the donor atom must possess a lone pair of valence electrons. In forming the bond, the number of valence electrons of the donor atom does not change, but the number of the acceptor atom is increased by 2. Hence, if the valence group of the donor atom is stable after coordination, it must have been stable before the bond was formed; in other words the donor atom must have formed part of a stable molecule or ion. It should be noted in this connection that Sidgwick's theory offers an explanation for one of the most troublesome aspects of Werner's theory—that molecules which are apparently saturated are still capable of further combination.

The acceptor atom, on the other hand, must have room in its valence group for 2 or more electrons. This may result in several different ways:

1. The acceptor atom may be an unsaturated, divalent atom such as sulfur or oxygen, which has only 6 electrons in the valence group.

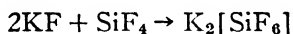


In such compounds the coordinate bond is very strong.

2. The acceptor atom may have an incomplete octet of shared electrons, such as in boron trichloride, BCl_3 , in which the boron atom has 6 shared electrons. An example of such coordination is the compound formed from boron trichloride and ammonia, $\text{H}_3\text{N} \rightarrow \text{BCl}_3$.

3. Stable cations, such as sodium or zinc ions, although they possess a complete outer group of 8 or 18 electrons, are capable of acquiring another complete and wholly shared valence group of 8 or more electrons. The positive charge of the ion promotes coordination by increasing the tendency to take up electrons.

4. A valence group of 8 electrons may expand with some atoms to accommodate 12 or even 16 electrons to form relatively stable structures. Thus, in the reaction



the silicon atom forms coordinate links with 2 fluorine atoms by expanding its octet to 12 electrons.

Recently several objections have been raised against the complete acceptance of the simple electron-pair bond theory described previously, but these are largely physical in character and do not prevent the theory generally from being extremely useful to the chemist. Its real value lies in the fact that it permits an understanding of the Werner concept, which in turn serves as a unifying principle throughout inorganic chemistry, and for this purpose it is not necessary that the exact character of the mechanism of chemical combination be known.

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CHAPTER III

CHELATE COMPOUNDS

IN THE early days of analytical chemistry, organic compounds were occasionally used for color reactions or for precipitating inorganic substances. For example, nitrites were detected and determined by the color reactions with primary aromatic amines and various coupling agents, and metals were precipitated as oxalates with oxalic acid or ammonium oxalate, or as hydroxides by means of organic bases. In 1905 Tschugaeff reported the use of dimethylglyoxime as a reagent for nickel, and later Brunck used this compound to effect many valuable separations. With the knowledge that dimethylglyoxime was a specific, or at least a highly selective reagent for nickel, and that it was an extremely sensitive reagent, many analytical chemists instituted a search for additional organic compounds which might prove superior in specificity and sensitivity to those then in use. This search was essentially empirical in character, since relationships between structure and analytical function were not then understood. Indeed today the investigation of organic compounds as analytical reagents has not completely passed the empirical stage, but many careful investigations have gradually revealed certain underlying principles which may be used in the search for new reagents and for the improvement of old ones.

The foundation for this search was laid with the announcement by Werner of his coordination theory which provides an excellent systematization of complex compounds. With the publication by Sidgwick of his electronic interpretation of the coordinate link, those groups capable of coordination became more clearly defined with the result that complex formation of certain ions or molecules could be predicted in advance. This development gave direction to the search for new analytical reagents, and eliminated much of the trial-and-error method previously employed.

Properties of inner-complex salts. Of surpassing value as analytical reagents are those organic compounds which are capable of forming chelate compounds with metals. The inner-complex salts, or chelate non-electrolytes, are particularly important. The properties of these compounds differ profoundly in many respects from normal salts, and certain of their characteristics make their formation of especial value in analytical chemistry. The more important of these are:

1. Most inner-complex salts are extremely insoluble in water, which makes possible many otherwise difficult quantitative precipitations.
2. They are usually soluble in non-polar solvents, and because of this property small quantities of metals can be extracted from aqueous solutions with immiscible liquids by first converting to an inner-complex salt.

3. In many cases the formation of inner-complex salts is accompanied by distinctive color changes, and many of these salts are intensely colored.

4. Reagents capable of producing inner-complexes are frequently specific or highly selective in their reactions with inorganic ions.

5. Precipitates formed in many cases are in suitable weighing form, and the ions to be determined are often a part of a heavy complex of extremely favorable conversion factor.

Groups essential to formation of chelate rings. THE search for new analytical reagents is primarily justified by the need for more sensitive and selective reactions. Since the almost limitless number of organic compounds offers the most fruitful field for search, analytical chemists are more and more turning to this source of material for new procedures. Of primary importance is the salt-forming ability of organic compounds, which, because of their structure, may also be capable of forming inner-complexes. Consequently it seems imperative first of all to review those structures possessed by organic compounds which render them useful as organic reagents.

It has been pointed out that among the organic compounds so far used, the most important are those containing salt-forming groups. The most common acidic radical occurring in organic compounds is the hydroxyl, OH, group. In most cases the ionization constant of organic hydroxyl compounds is very small, but for the most part molecules containing this group are capable of forming metallic salts. In addition to alcohols, phenols, and certain enolic compounds, many other well known acidic compounds may be regarded as containing the hydroxyl radical joined to the hydrocarbon nucleus through the agency of some other group. For example, the carboxyl group may be regarded as formed by inserting the carbonyl radical between the hydroxyl group and the organic radical. Similarly, when N, NO, SO, SO₂, As, or AsO groups join hydroxyl and organic radicals, the oxime or enolic form of the nitroso group (N—OH), nitroxyl or enolic form of the nitro group (NO—OH), sulfinic acid (SO—OH), sulfonic acid (SO₂—OH), arsenic acid (As(OH)₂), or arsonic acid —AsO(OH)₂ groups, respectively, are formed. Phosphorus may behave like nitrogen, but the phosphonic, phosphinic and phosphinous acids have not yet been applied to analytical procedures.

Another group of acidic compounds contain the thioalcohol or mercapto group, SH. Although the thioalcohols are generally more strongly acidic than the corresponding oxygen compounds, fewer members of this class are known. As with alcohols, the thioalcohols yield other classes of acidic substances by the interposition of carbonyl or thiocarbonyl groups. In the former case, mono-thiocarboxylic acids are formed, whereas in the latter the products are dithiocarboxylic acids. Other acids which contain, in addition to the thioalcohol group, nitrogen, phosphorus, arsenic and sulfur have not been investigated.

The only other radical which appears to impart acidic properties to organic molecules is the imino, or NH group. This is the weakest of the acid groups, and occurs in only a few compounds of analytical importance. Other possible acids may be formed by replacing the nitrogen atom with phosphorus or arsenic, but these have not been investigated.

To summarize, then, the acid groups most frequently responsible for salt formation in organic compounds are:

$-\text{CO}_2\text{H}$	(carboxyl)
$-\text{SO}_2\text{H}$	(sulfinic)
$-\text{SO}_3\text{H}$	(sulfonic)
$-\text{OH}$	(hydroxyl)
$-\text{SH}$	(mercapto)
$-\text{NOH}$	(oxime)
$-\text{NO}-\text{OH}$	(nitroxyl)
$=\text{NH}$	(imine)
$-\text{As}(\text{OH})_2$	(arsinic)
$-\text{AsO}(\text{OH})_2$	(arsonic)

To this list of salt-forming groups should also be added the amine group and the substituted amines which are capable of forming salts with acids.

Many analytical applications of acidic organic compounds are known in which normal salts are formed, as in the precipitation of metallic oxalates, but the value of the reagent is immeasurably enhanced if in addition to the acidic group these molecules possess a structure which makes possible the formation of a coordinate bond with the metal atom so as to form a cyclic structure. As a rule coordinating structures contain oxygen, sulfur or nitrogen atoms, and these are usually found in the carbonyl ($=\text{CO}$), thiocarbonyl ($=\text{CS}$), primary amine ($-\text{NH}_2$), secondary amine ($-\text{NHR}$), tertiary amine ($-\text{NR}_2$), nitroso ($-\text{NO}$) and nitro ($-\text{NO}_2$) groups. In addition, nitrogen atoms or doubly linked carbon atoms of open or closed chains give rise to coordination.

Baeyer's strain theory. In addition to the character of the groups present in an organic compound, chelation also depends to a very large extent upon the relative positions which they occupy in the molecule. In general, the groups must be so located with respect to one another that the ring which they form will contain not less than 3 or 4 and not more than 7 or 8 atoms. In fact, most rings contain 4, 5 or 6 atoms.

In selecting organic compounds which might be expected to yield chelate rings with metallic ions, the positions of the salt-forming and coordinating groups may be determined by applying the principle of the Baeyer strain theory. Consequently, it is necessary first of all to consider briefly the essential features of this theory. This theory is based on the assumption that the angle between 2 of the valence bonds of an atom has a natural value which is determined by an atomic model, and any departure of the angle from this value gives rise to a corresponding strain or instability of the molecule. Many of the common elements like carbon behave as regular tetrahedra with their nuclei at the centers, and their valence forces directed toward the apices or corners. These elements include those belonging to the first period in the periodic classification, as well as silicon, phosphorus, sulfur, copper, zinc, arsenic, selenium and tin.

The angle formed by the lines joining the center and 2 apices of a regular tetrahedron is $2 \tan^{-1} \sqrt{2} = 109^\circ 28'$. When 2 atoms are joined by a single covalent bond, the valence forces operate along a straight line joining the centers

of 2 such tetrahedra and passing through their 2 respective coinciding apices. The angle formed between two such bonds is also $109^{\circ} 28'$.

When 2 atoms are joined by 2 covalent bonds, the tetrahedral figures are regarded as having an edge in common. In this case the angle between the lines representing valence forces will be that formed by a line from the center and perpendicular to the common edge and another line from the center and passing through one of the other apices. This angle is $180^{\circ} - \tan^{-1} \sqrt{2} = 125^{\circ} 16'$. Assuming that the atoms of cyclic structures lie in the same plane, 3-, 4-, 5-, 6-, 7- and 8-membered rings, respectively, would be represented by corresponding polygonal figures. The angles of regular polygons having 3, 4, 5, 6, 7 and 8 sides have values of 60° , 90° , 108° , 120° , $128^{\circ} 34' 17''$, and 135° , respectively. Thus, if atoms are joined to form a 3-membered ring, the natural valence angles must be reduced by $109^{\circ} 28' - 60^{\circ} = 49^{\circ} 28'$ if all bonds are single bonds, and by a greater amount if a double bond is formed. This large deflection from the natural angles which would be necessary for the formation of a 3-membered ring would cause such a compound to be very unstable. Actually, no 3-membered ring of analytical significance has been reported.

It should be emphasized that the actual strain in cyclic structures cannot always be stated with certainty. This is particularly true when the ring contains both single and double bonds, because it is then difficult to determine whether the strain is distributed equally around the ring, with consequent departure from regularity, or whether alternatively, the larger angle undergoes greater deflection than the smaller angle in order to maintain regularity.

Further, the problem of strain is complicated by the fact that the strains may be influenced by the size of the atoms comprising the cyclic structure. Ingold¹ has proposed a modification of Baeyer's theory. According to Ingold the tetrahedron can be regarded as regular only when the carbon atom (or other atom showing the tetrahedral type of symmetry) is joined to 4 atoms of the same size, and the angle between 2 valence bonds forming part of the ring will vary according to the nature of the 2 atoms attached to the carbon (or other) atom.

It appears probable that since different atoms have different covalent radii, the distribution of strain among the various angles of a cyclic structure will vary for rings of the same size depending on the nature of the atoms of which they are composed. The covalent radii for a number of common atoms are given in Table 4.

In the simple strain theory it is assumed that all atoms are of the same size, and this is very nearly true of all those atoms most frequently found in chelate rings, such as carbon, nitrogen and oxygen. The heavier atoms which occur in many chelate rings are larger, but the ease with which such rings are formed when the heavy metal atoms are replaced by hydrogen suggests that atomic size is not of primary importance.

In general, then, it may be said that it appears likely that not all rings of a given number of atoms are identical. Average values for bond angles should, however, approximate the natural bond angles calculated as described previously. That this is true is attested by the close agreement of the strain theory with the known characteristics of cyclic compounds.

For 4-membered rings containing only single bonds, the average deflection from the natural angle is $109^{\circ} 28' - 90^{\circ} = 19^{\circ} 28'$, a value considerably less than that for a 3-membered ring and thereby indicating a greater stability. This, of course, is in agreement with fact. With one double bond the deflection is $27^{\circ} 22'$ and with two double bonds $35^{\circ} 16'$. A few 4-membered rings having not more than one double bond have been reported.

TABLE 4.—COVALENT RADII

Element	Single Bond Å	Double Bond Å
Boron	0.88	0.76
Carbon	0.77	0.66
Nitrogen	0.70	0.60
Oxygen	0.66	0.55
Silicon	1.17	1.07
Phosphorus	1.10	1.00
Sulfur	1.04	0.94
Germanium	1.22	1.12
Arsenic	1.21	1.11
Selenium	1.17	1.07
Tellurium	1.37	1.27

For 5-membered rings containing only single bonds, the average decrease in the bond angles is $109^{\circ} 28' - 108^{\circ} = 1^{\circ} 28'$. For one double bond the deflection is $7^{\circ} 47'$ and for two double bonds $14^{\circ} 6'$. For 6-membered rings the average increase in deflection is $120^{\circ} - 109^{\circ} 28' = 10^{\circ} 32'$ when no double bonds are present. With one double bond the average increase is $5^{\circ} 16'$. The deflection is 0° with two double bonds and an average decrease of $5^{\circ} 16'$ with three double bonds. The comparatively small strain in 5- and 6-membered rings containing one or more double bonds indicates a greater stability for these structures, and this is reflected in the large number of compounds containing these groups.

In 7-membered rings an average increase in the bond angles of $19^{\circ} 6'$, $14^{\circ} 35'$, $10^{\circ} 5'$ and $5^{\circ} 34'$ is necessary if no double bond, one double bond, two double bonds or three double bonds, respectively, are present. For 7-membered rings containing double bonds the deflection is not unusually high, and this is confirmed by the existence of several such compounds. For 8- and 9-membered rings, however, the average angular increase would necessarily be quite high, and in consequence few such rings are known.

The data on bond angles in rings of different size and having different numbers of double bonds is summarized in Table 5.

Although the Baeyer strain theory provides an excellent basis for the study of ring structures, it must be borne in mind that the deflection of the bond angles and the strain thus developed is calculated on the assumption that the atoms of the cyclic group lie in the same plane. Rings of 7 or more atoms, however, may attain a strainless condition if 1 or more of the atoms lies outside

of the plane occupied by the others. Indeed, essentially strainless rings containing as many as 32 atoms have been prepared.

TABLE 5.—AVERAGE STRAIN PER ATOM IN RINGS

No. of Atoms in Ring	Number of Double Bonds				
	0	1	2	3	4
3	49°28'	60°0'			
4	19°28'	27°22'	35°16'		
5	1°28'	7°47'	14°6'		
6	—10°32'	—5°16'	0°0'	5°16'	
7	—19°6'	—14°35'	—10°5'	—5°34'	
8	—25°32'	—21°35'	—17°38'	—13°41'	—9°44'
9	—30°32'	—27°1'	—23°31'	—20°0'	—16°29'

It is also important to remember that the basic assumption of the strain theory is that atoms conform structurally to a tetrahedral symmetry, but considerable evidence has been offered to show that this is not strictly true. Pauling² for example, reports that the natural bond angle for oxygen and sulfur may often be more nearly 90° than 109° 28'. It is also known that substituent groups and other adjacent ring structures with atoms in common may alter conditions of strain; hence, attention must be directed to the entire molecule rather than merely to the groups capable of chelation. In many chelate compounds one of the bonds between the metallic atom and the organic group is electrovalent and consequently non-directional in character. Although this does not necessarily mean that conditions of symmetry previously discussed do not apply, it does appear probable that the other angles of the ring are subjected to less strain because of this difference in character.

Finally, the formation of chelate ring systems depends to a very large extent on the character of the metal atom which forms a part of the ring. For example, while the copper salt of aminoacetic acid is a typical inner-complex, the corresponding zinc and cadmium salts apparently are not, since their solutions are non-conducting. This appears the more unusual in view of the fact that numerous coordination compounds of ammonia and zinc and cadmium salts are known.

Evidence for the existence of chelate rings. In many of the reactions used in the development of analytical procedures, it becomes a matter of considerable importance to determine whether chelation occurs or whether products formed are true salts. For this reason the evidence for or against the existence of chelate rings is important in conducting research in the field of organic analytical reagents.

Briefly, the most important facts upon which the existence of chelate rings has been based are:

1. Thousands of coordination compounds are known in which the coordination numbers of the metals involved are invariably 4 or 6, and yet only 2 or 3

molecules of organic compounds containing two associating structures unite with such metals. Therefore, if all coordinate positions are to be occupied, and the compound is assumed to be monomolecular, the linking of all 4 or 6 units with consequent ring formation must occur.

2. Reactions which normally reveal the presence of certain metals fail in solutions of their complex salts, thus indicating the absence of simple ions of the metal. This is further confirmed by conductivity measurements which prove the complex to be a non-electrolyte, anion or cation as calculated assuming chelation occurs.

3. Chelate compounds are saturated and do not add other groups such as ammonia.

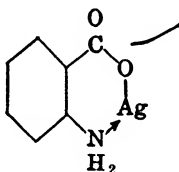
4. On the basis of chelate structures certain isomers are predictable, and such predictions have been realized in many instances.

5. Chelation is seen in certain cases to yield asymmetric structures, and proof of this is found in the resolution of many metallic compounds of this type.

6. Functional groups which are involved in chelation are non-reactive. For example, the carbonyl group of the acetylacetonates does not react with phenylhydrazine, and the amino group of the copper salt of aminoacetic acid cannot be acetylated.

7. Chelate compounds are formed only with organic molecules having functional groups in such positions as to yield rings of from 4 to 7 members.

8. Functional groups responsible for ring formation take part equally in reactions which result in opening the ring. For example, in the reaction of the silver salt of anthranilic acid



with ethyl iodide, both the ester, $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CO}_2-\text{C}_2\text{H}_5$, and the amine derivative, $\text{C}_2\text{H}_5-\text{NH}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$, are formed.

Properties of inner-complex compounds. Chelate compounds containing a coordinate link, and especially inner-complex salts, can be distinguished from true salts by the difference in properties exhibited by these two classes of compounds. The peculiar properties associated with the coordinate link depend on the fact that the link generally is broken more easily than a normal covalence, and that its formation brings about an electrostatic disturbance within the molecule, and consequently a stronger external field.

The more important properties useful in differentiating chelate structures which are formed by coordination are:

1. *Volatility.* The effect of the large external electrical field of ionized molecules in holding the molecules together is reflected in the low volatility of these substances. A similar, but smaller, effect is observed in compounds containing a coordinate link. In general, then, the boiling points of compounds

containing a coordinate link are higher than of isomeric compounds containing normal covalences.

2. *Dielectric constant.* The dielectric constant is a measure of the work done by an external electrical field in orienting the molecules against the effect of their thermal agitation. The magnitude of the dielectric constant, therefore, depends on the dipole moment of the molecules. Compounds containing no coordinate linkages, such as the hydrocarbons, ethers and esters have very low dielectric constants, ranging from 2 to approximately 7. Compounds containing a coordinate link have higher dielectric constants, but not so high as electrolytes. The dielectric constant for nitromethane, for example, is approximately 39.

3. *Solubility.* Inner-complex salts are usually only very slightly soluble in water, but quite soluble in hydrocarbons and other organic solvents. This behavior generally is in contrast to that of true salts which are more frequently soluble in water, but insoluble in organic liquids.

4. *Parachor.* The molecular volume of a compound is affected by intermolecular attraction caused by the external electric field. An ionic bond leads to a considerably smaller molecular volume than a normal covalency, and, as expected, the semi-polar coordinate bond has an effect which is intermediate in magnitude between these two. This effect is small, however, and cannot be determined without an accurate means of calculating the contribution of each atom to the molecular volume. Kopp studied the molecular volume of liquids and determined the density at the boiling point. The boiling points are, according to Guldberg's rule, approximately two thirds of the critical temperature, and therefore represent corresponding states. The determination of density at correspondingly states eliminates variations caused by intermolecular forces. Traube³ attempted to eliminate intermolecular forces by measuring the partial molal volumes of substances in dilute solutions of inert solvents.

Sugden⁴ has developed another method of accounting for inter-molecular forces in calculating additive and constitutive factors of molecular volume. He has pointed out that in calculating the molecular volume, allowance should be made for the effect of the very large internal pressure of liquids, which is manifested in surface tension. Macleod⁵ discovered that surface tension and density are related by the following empirical expression:

$$\gamma = C(D - d)^4$$

or

$$C^{\frac{1}{4}} = \frac{\gamma^{\frac{1}{4}}}{D - d}$$

in which D and d are the densities of liquid and vapor, respectively, at any given temperature, and C is a constant. Sugden multiplied this equation by M , the molecular weight, and obtained

$$\frac{M\gamma^{\frac{1}{4}}}{D - d} = MC^{\frac{1}{4}} = P \text{ (a constant)}$$

where P is called the *parachor*. The parachor may be regarded as the molecular volume measure at a standard internal pressure.

The analysis of parachor values has proved highly successful. These values show the same kind of additive and constitutive relations as those of the uncorrected molecular volume. The value for a particular molecule is found to be equal to the sum of the number of terms for the constituent atoms, in addition to other terms for particular types of linkage, such as a double bond, a triple bond, a 6-membered ring, etc.

The values for some of the common elements and also for some of the constitutive influences are shown in Table 6.

TABLE 6.—PARACHORS

Atomic		Constitutive	
Element	Parachor	Structure	Parachor
Hydrogen	17.1	Covalent double bond	23.2
Carbon	4.8	Covalent triple bond	46.4
Nitrogen	12.5	Coordinate bond	-1.6
Oxygen	20.0	3-Membered ring	16.7
Fluorine	25.0	4-Membered ring	11.6
Silicon	12.0	5-Membered ring	8.5
Phosphorus	39.2	6-Membered ring	6.1
Sulfur	48.2	7-Membered ring	4.6
Chlorine	54.3	8-Membered ring	2.4
Bromine	68.0	Naphthalene ring	12.2
Iodine	90.0	O ₂ in esters	60.0
		Two O-atoms and 1 double bond (theory)	63.2

A study of many compounds containing one double bond revealed that they fell into two groups on the basis of parachor values: for many substances containing the groups C=C, C=O, C=S and N=O an increase of 23.2 units was observed for the double bond, whereas with others a decrease of 1.6 units was noted. This difference lies well outside the limits of experimental error, and the distinction is quite sharp without intermediate values. Thus, it is apparent that the double bond of classical formulas in reality represents two kinds of linkage, the one being the true double bond of 4 shared electrons and the other the coordinate link of 2 shared electrons. The parachor provides a means of distinguishing between them: molecules which show an increase of 23.2 units contain the true double bond, whereas those which show a decrease of 1.6 units contain a coordinate link.

Although the parachor has been of great value in determining organic structures, these values have been determined for only a few metallic elements because of the difficulty in obtaining liquid compounds containing them.

1. C. K. Ingold, *J. Chem. Soc.*, 119, 305 (1921).
2. L. Pauling, *J. Am. Chem. Soc.*, 53, 1367 (1931).
3. Traube, *Samml. Chem. Chem.-tech. Vorträge*, 4, 255 (1899).
4. Sugden, *The Parachor and Valency*, Routledge and Sons, Ltd., London (1930).
5. D. B. Macleod, *Trans. Faraday Soc.*, 19, 38 (1923).

CHAPTER IV

TYPES OF CHELATE RINGS

ORIGINALLY the term chelate was proposed by Morgan¹ to designate those cyclic structures which are formed by the union of metal atoms with organic or inorganic molecules (page 12). The formation of these rings may involve either primary or secondary valence. Primary valence as used here denotes that in the formation of the valence bond there is replacement of a hydrogen atom. In the formation of a secondary valence bond there is no such replacement. Eventually the expression chelate ring was extended to include rings formed by 2 primary valences, 1 primary and 1 secondary, and by 2 secondary valences.

Sidgwick² has proposed a convenient classification of chelate rings into three types, which are based on the character of the bonds present in the cyclic system. Rings in which the coordinate link becomes identical with a normal covalent bond as a result of chelation are designated as Type A. Rings containing one definite coordinate bond are denoted as Type B, and those containing two coordinate links as Type C. It should be pointed out that these types are not always sharply differentiated, and there is evidence that in the liquid state and in solutions the chelate structure exists in equilibrium with a non-chelate system.

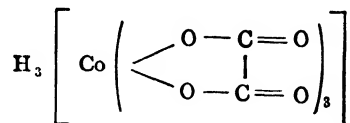
Compounds of Type A

Rings of Type A are formed by the replacement by a metal of 2 hydrogen atoms of a dibasic acid. These structures are usually quite stable; and, in addition to the common 5- and 6-membered rings, may contain cycles of 4 and 7 members, which are found only infrequently in other types of chelate rings. These compounds may be called coordination compounds of ions, since upon dissociation they normally form ions. For example, the beryllium salt $K_2[Be(C_2O_4)_2]$ yields both beryllium and oxalate ions.

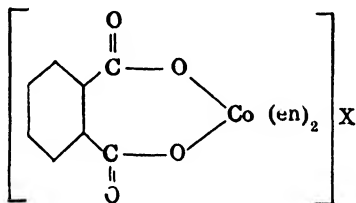
Many compounds possess structures capable of forming chelate compounds of Type A. The following classes are most frequently encountered.³

(a) **Inorganic dibasic acids.** Many compounds are known in which various bivalent inorganic anions occupy two positions in the coordination sphere surrounding a metal atom. Typical of these are carbonate, sulfate, sulfite, thio-sulfate, selenate, selenite, chromate and molybdate. As a rule compounds containing chelating bivalent anions contain only one such group as in $[(NH_3)_4-CoCO_3]X$, but some compounds, such as $Na_3[Fe(SO_4)_3]$, are known which contain three such groups to complete the coordination number of 6 by bivalent groups alone. The positions occupied in the coordination sphere by these bivalent radicals are considered to be adjacent or *cis*-positions, since the groups are not large enough to span the axial or *trans*-positions.

(b) **Organic dibasic acids.** Chelate rings resulting from reactions involving organic dibasic acids are well represented by the oxalato compounds, in which the oxalate radical occupies two positions in the coordination sphere about the metal atom. As a result, well-defined, stable 5-membered rings are formed. Many examples of this type are known involving metals of coordination numbers 4 and 6, and in which the metal atom may be a part of 1, 2 or 3 rings. Typical of these are the salts of the acid

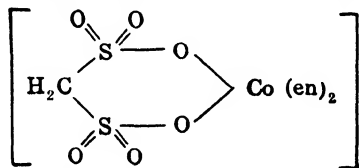


Similar compounds containing 6-membered rings are formed with malonic acid. With the higher homologs, which would yield 7- or 8-membered rings, no compounds are known in which the metal atom is a part of more than one such ring. Phthalic acid yields crystalline compounds containing a 7-membered ring.⁴



Homophthalic acid yields similar 8-membered rings.⁴

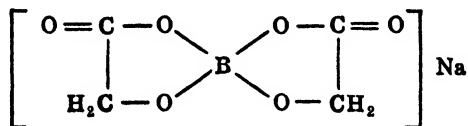
✓ (c) **Disulfonic acids.** Price and Duff⁵ have shown that methionic acid may give rise to chelate rings by preparing the compound.



Aromatic o-disulfonic acids appear to function similarly.⁴

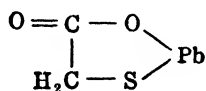
(d) **Carboxy sulfonic acids.** A number of chelate structures have been formed from compounds containing one carboxyl and one sulfonic acid group.^{4,5,6}

(e) **Hydroxy carboxylic acids.** In only a few cases has it been possible to assign definite structures to the metallic complexes of the aliphatic hydroxy acids. Toward boron, however, glycolic acid functions dibasically to yield compounds of the type.^{7,8}



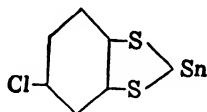
The complex copper compounds of glycolic and lactic acids are stable only in the presence of salts of the acids. Many very stable cyclic compounds of salicylic acid are known. Similar complexes are obtained with mandelic acid. Hydroxy and dihydroxy dibasic acids, such as malic and tartaric acids also form very stable complexes. These are best known as the copper complex in Fehling's solution and the antimony complex in tarter emetic.

(f) **Mercapto carboxylic acids.** Certain compounds are known in which mercapto carboxylic acids function dibasically to form chelate compounds.^{9,10} Among the best known of these are the metallic derivatives of thioglycolic acid and the mercapto propionic acids. In the lead salt of thioglycolic acid



the coordination sphere does not appear to be filled.

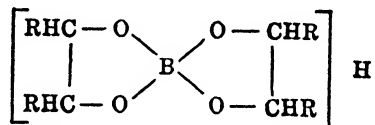
(g) **Dimercapto compounds.** Stannous tin forms salts with 4-chloro-1,2-dimercaptobenzene and toluene-3,4-dithiol in which both mercapto groups appear to function as acids, whereby stable 5-membered rings are formed^{11,12}



The enolic form of dithiooxalic acid similarly forms a cyclic compound with nickel.^{13,14}

(h) **Diamides.** Compounds containing two amide groups are often found to function dibasically to form chelate compounds.¹⁵⁻²⁸ Among the compounds which form such metallic complexes are malonamide and oxamide. It is not known whether the acid amide form or the acid imide tautomer is the active form.

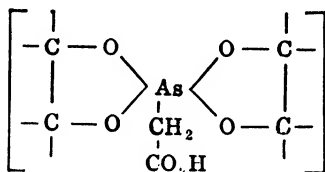
(i) **Dihydroxy compounds.** Certain 1,2-glycols form 5-membered chelate rings in aqueous solutions of boric acid.



The effect of chelation is to cause a large increase in the strength of the acid due to the greater stability of the chelate anion. The position of the hydroxyl groups has a pronounced influence upon the effect produced. For example, hydroxyl groups on neighboring carbon atoms and in the same plane produce the maximum increase in the conductivity of boric acid solutions.²⁸ The *cis*-form of cyclopentandiol-1,2 increases the strength of boric acid, but the *trans*-form does not. The significance of spatial configuration and constitution of the

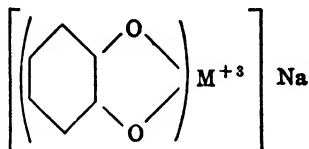
glycols in their action on boric acid is not clear, since compounds such as ethylene glycol, 1,2-propylene glycol and pinacol have no effect on boric acid, and in some cases both pairs of optical isomers or of *cis-trans* isomers produce the same effect.^{29,30,31}

The 1,2-glycols also form chelate compounds with arsenic acid and with arsenoacetic acid.^{32,33} The type of compound formed may be represented as follows:



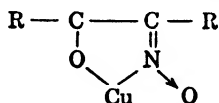
Polyhydroxy compounds frequently prevent the precipitation of metallic hydroxides by sodium or potassium hydroxide, although the character of the complex formed has not been definitely established.^{34,35,36}

The more strongly acidic diphenols give rise to more definite and stable metallic complexes. Pyrocatechol, for example, forms many well-defined compounds with metals of coordination numbers of 4 and 6. Compounds of pentavalent arsenic and antimony^{37,38,39} and trivalent arsenic and antimony⁴⁰ have been prepared.



Alizarin forms metallic derivatives by acting as a dibasic acid. The alkali metal salts of the complex acid with ferric iron, $[(\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_2\text{O}_2)_3\text{Fe}]\text{H}$, have been prepared.⁴¹

(j) **Hydroxy oximes.** The α -acyloin oximes, having the general formula $\text{R}-\text{CH}(\text{OH})-\text{C}(=\text{NOH})-\text{R}$, react toward copper as dibasic acids to form green, insoluble copper salts corresponding in composition to



α -Benzoin oxime is typical of this group, and has been widely used in the analysis of copper. For a further discussion of these interesting compounds, see section on oximes.

When the hydroxyl and oxime group are separated by an intervening carbon atom, as in the compound $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{C}(=\text{NOH})-\text{CH}_3$, the reaction with copper is no longer obtained.

Compounds of Type B

In systems of this type an atom is bound in the ring on one side by a normal covalent bond and on the other by a coordinate link. Rings of this type are usually less stable than those of type A, and they always contain 5 or six members. Structures most frequently found are 5-membered rings containing one double bond and 5- and 6-membered rings containing two double bonds. The conjugated, 6-membered rings of this class are perhaps the most common of all chelate structures.

Atoms occurring in these rings, other than a metal and hydrogen, are carbon, nitrogen, oxygen and occasionally sulfur. Since the metal is not linked to carbon, and sulfur is seldom present, the number of types of ring structures is somewhat limited. The most common of the structural groups which are capable of forming 6-membered rings with metals are:

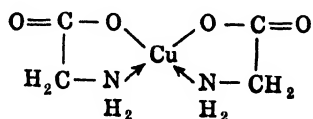
- (I) $\text{HO}-\text{C}=\text{C}-\text{C}=\text{O}$
- (II) $\text{HO}-\text{N}-\text{C}-\text{C}=\text{O}$
- (III) $\text{HO}-\text{C}=\text{C}-\text{N}=\text{O}$
- (IV) $\text{HO}-\text{N}=\text{C}-\text{C}=\text{NX}$
- (V) $\text{HO}-\text{C}-\text{C}-\text{N}=\text{N}$
- (VI) $\text{HO}-\text{N}=\text{N}-\text{C}=\text{N}$

Representative compounds containing or capable of forming these structures by classes are:

- (I) β -Keto esters (acetoacetic acid); β -diketones (acetylacetone); α -dicarboxylic esters (ester of malonic acid); salicylic acid; 1-hydroxynaphthoquinone; 1-hydroxyanthraquinone; o-hydroxyacetophenone.
- (II) Orthoquinoneoximes; o-nitrophenol; monoximes of α -diketones; oximes of α -ketonic esters.
- (III) α -Nitroso- β -naphthol.
- (IV) Dioximes of α -diketones (dimethylglyoxime).
- (V) Azo dyes having a hydroxy group in the ortho position to the azo group.
- (VI) Enol form of nitrosoguanidine.

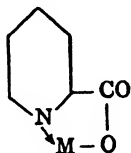
Many combinations of acidic and coordinating groups give rise to a wide variety of chelate structures of Type B. The most common of these are:

(a) **Aminoacids.** α -amino acids form metal salts which have been shown to be inner-complex compounds.⁴²⁻⁴⁶ Typical of these is the copper salt of α -aminoacetic acid (glycine).

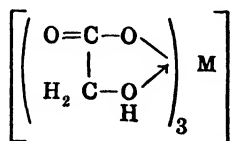


β -Amino acids form similar cyclic compounds with metals, but these contain 6-membered rings. Chelation does not occur, however, with γ -, δ - or ϵ -amino acids.

Acids having an adjacent cyclic nitrogen atom, as in α -picolinic and quinaldic acids similarly form rings with metals.

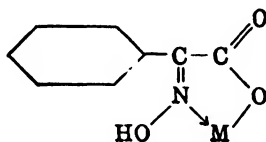


(b) **Hydroxy carboxylic acids.** Although considerable confusion exists regarding the exact character of the metallic derivatives of aliphatic hydroxy acids, there is evidence that the hydroxyl group may function as an acid or as a coordinating structure. Conductivity measurements of the rare earth glycolates and lactates indicate that at least partial chelation of the



type occurs.⁴⁴⁻⁴⁹ Replacement of the hydrogen atom of the hydroxyl group by a methyl or phenyl radical does not alter the salt-forming properties of these compounds.

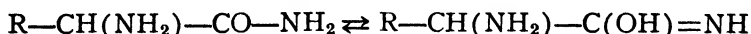
(c) **Compounds containing the carboxyl and oxime groups.** The oxime of phenylglyoxylic acid forms metallic compounds.⁵⁰ The β -form of the oxime reacts instantly to form compounds of the type



The β -form is assigned the *syn*-phenyl configuration. The α -isomer forms complexes only slowly, and with simultaneous conversion to the β -modification.

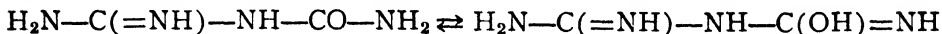
(d) **Carboxylic acid derivatives of thioethers.** Ethyl thioglycolic acid yields a chelate compound with platinum in which the sulfur atom is the coordinating structure.

(e) **Amine derivatives of acid amides.** α -amino acid amides form copper compounds which exhibit typical properties of inner-complex compounds.^{51,52} It is not known whether hydrogen is replaced from the amide group or from the hydroxyl radical of the tautomeric imide. The equilibrium between these forms is represented by the following equation:

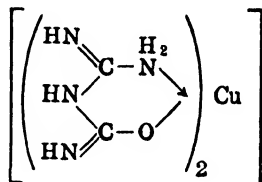


The nitrogen atom of the α -amine group coordinates to the metal to form the ring.

Dicyanodiamidine (guanylurea) and biguanidine form similar copper compounds.^{53,54} Dicyanodiamidine exists in two tautomeric forms,



which make possible the existence of three forms of the copper complex. The copper atom may replace one hydrogen atom of the amide group or the hydrogen atoms of the enolic hydroxyl radical or the imide group formed by enolization.



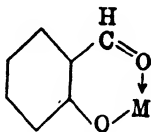
Two possible structures have been assigned to the copper salt of biguanide, $\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{NH}-\text{C}(=\text{NH})-\text{NH}_2$.

(f) **Amino sulfonic acids.** Aminomethylenesulfonic acid forms a copper salt which has been assigned a chelate structure.⁵⁵

(g) **Dihydroxy compounds.** The monovalent thallium compound of 2,2'-biphenol apparently is a coordinate structure in which one hydroxyl group is acidic and the other coordinating.

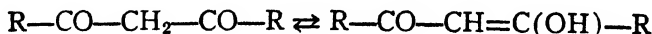
Reihlen,⁵⁶ Weinland and Walter⁵⁷ and Karrer⁵⁸ have studied the red iron complex of pyrocatechol and have found it to be the tripyrocatechate ferric anion, $[(\text{C}_6\text{H}_4\text{O}_2)_3\text{Fe}]^{-3}$, in which one of the iron-oxygen bonds is formed by replacement of the hydrogen atom of one hydroxyl group and the other oxygen atom is coordinatively linked to the metal.

(h) **Hydroxy carbonyl compounds.** Aromatic o-hydroxy aldehydes and o-hydroxy phenones are capable of forming chelate compounds through coordination of the carbonyl oxygen atom. Salicylaldehyde, for example, forms numerous metal compounds of the type.

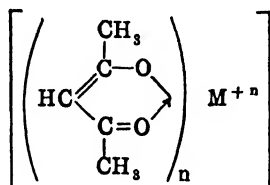


They are not very stable toward water, but may be formed in organic solvents. Cobalt, copper and nickel derivatives of p-methoxy-o-hydroxyacetophenone have also been prepared.⁵⁹

Another important group of hydroxy carbonyl compounds are the 1,3-diketones, which form metallic salts through enolization.

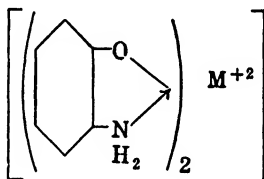


Best known of this group is acetylacetone, which has been extensively studied. Many acetylacetonates have been prepared, and most of these are non-electrolytes.^{60,61} These compounds have the following structure:

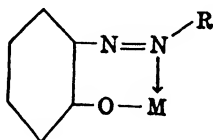


The boron, silicon and titanium compounds correspond to the formulas $[(\text{acac})_2\text{B}]\text{X}$, $[(\text{acac})_3\text{Si}]\text{X}$, $[(\text{acac})_3\text{Ti}]\text{X}$, in which acac = the anion of acetylacetone.

(i) **Amino hydroxyl compounds.** Some evidence has been offered to show that monoethanolamine forms chelate compounds by coordination of the amino nitrogen atom with the metal.^{62,63} Amino phenols form more definite and stable compounds. o-Aminophenol forms copper, nickel, zinc and cadmium derivatives which are typical inner-complex compounds



(j) **Hydroxy azo compounds.** Azo dyes containing an hydroxyl group in the ortho position to the azo group, —N=N— , are capable of forming chelate rings of the type



Such compounds are not formed when the hydroxyl group is in the meta or para position. Formation of these compounds is offered as an explanation of mordant dyeing.

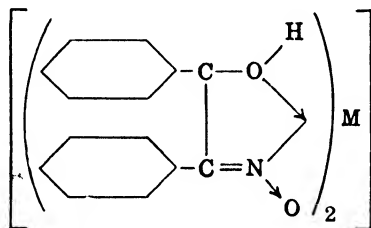
The cupric, nickel and cobaltic compounds of ortho monohydroxyazo compounds are typical inner-complex compounds. The blue magnesium lake with p-nitrobenzeneazoresorcinol, which is used as a test for magnesium, is in all probability due to the formation of a compound of this type.

(k) **Hydroxy derivatives of cyclic nitrogen compounds.** Chelate compounds are formed by replacement of the hydrogen atom of an hydroxy group suitably attached to a heterocyclic nitrogen compound. Among the most impor-

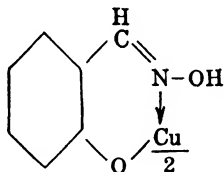
tant of these compounds are the metallic salts of 8-hydroxyquinoline and its derivatives. For a more detailed discussion of these compounds, see section on 8-hydroxyquinoline.

(l) **Hydroxy oximes.** Acyloin oximes, which contain both the hydroxy and oxime groups, form chelate compounds by the replacement by the atom of a metallic element of the hydrogen atoms of both acidic groups. These compounds belong to Type A.

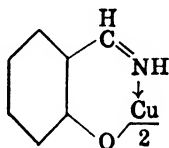
α -Benzoinoxime, however, acts toward nickel, palladium and bivalent platinum as a monobasic acid to form typical inner-complex compounds of the type



The aryl aldioximes and aryl ketoximes containing an ortho hydroxyl group form copper compounds in which the copper atom replaces the hydroxyl hydrogen atom, and is in turn coordinated to the oxime nitrogen atom. The copper compound of salicylaldoxime, which is the best known representative of this class, has the following composition:



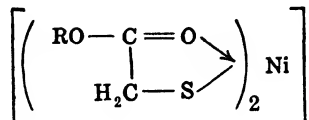
(m) **Hydroxy aldimines and hydroxy ketimines.** Nickel salts react with o-hydroxy aldehydes in aqueous ammonia to form nickel salts of hydroxy-aldimines.^{64,65,66}



Similar compounds have been prepared with copper, zinc, palladium and other metals. Ortho hydroxy ketones react to form the same type of compounds.

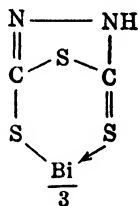
(n) **Mercapto carbonyl compounds.** Thioglycolic acid forms chelate compounds by the replacement of the hydrogen atom of the mercapto group with a metal and coordination of the metal with the oxygen atom of the carbonyl

group. Similarly, the esters and amides of thioglycolic acid form metallic derivatives of the type

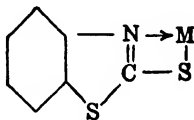


One of the most useful analytical reagents of this group is thionalide (thioglycolic β -aminonaphthalide), which forms many metallic derivatives.

(o) **Mercapto thiocarbonyl compounds.** Bismuth forms a chelate compound with 2,5-dimercapto-1,3,4-thiodiazole by the replacement of the hydrogen atom of one of the mercapto groups and coordination of the metal atom with the sulfur atom of a thiocarbonyl group formed by enolization.⁶⁷

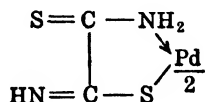


(p) **Mercapto derivatives of heterocyclic nitrogen compounds.** 2-benzothiazolethiol forms chelate compounds by the replacement of the hydrogen atom of the mercapto group and coordination of the metal atom with the nitrogen atom of the thiazole ring.



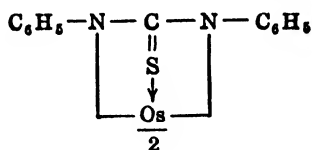
Similar compounds are formed with 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolon-2.

(q) **Mercapto thioamides.** Palladium forms a chelate compound with rubeanic acid. Although several possible structures may be assigned this compound, since the reagent exists in a number of possible tautomeric forms, some evidence indicates that the metal replaces the hydrogen atom of a mercapto group, and is coordinated with the nitrogen atom of the thioamide group.^{68,69}

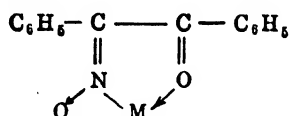


(r) **Mercapto imide derivatives.** The enolized form of rubeanic acid, $\text{HN}=\text{C}(\text{SH})-\text{C}(\text{SH})=\text{NH}$, forms salts with metals by replacing the hydrogen atoms of the mercapto groups and coordinating with the imide nitrogen atoms.

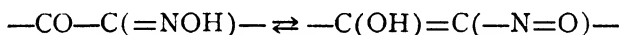
(s) **Thiocarbonyl imide derivatives.** The osmium derivative of thiocarbonyl imide has been assigned the following formula:



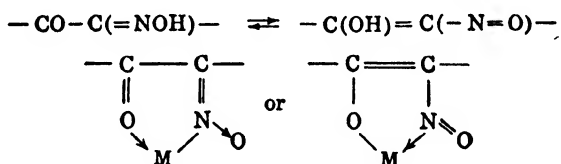
(t) **Oxime carbonyl compounds.** The monoximes of diketones, such as α -benzilmonoxime, form metallic derivatives of the type



In compounds of this type the nitrosophenol group is tautomeric with the diketone monoxime group



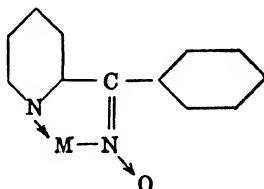
so that it is difficult to determine which of the two structures is responsible for ring formation. Thus, the metallic derivatives may be represented as



Analytically important compounds which belong to this class are the isomeric nitrosonaphthols, 2-isonitrosoketotetralin, cupferron and neocupferron.

(u) **Dioximes.** The dioximes of the α,β -diketones form metallic derivatives in which one of the oxime groups functions as an acid and the other as a coordinating structure. Best known of these compounds are dimethylglyoxime, α -furildioxime and cyclohexanedionedioxime. For a complete discussion of these compounds, see section on oximes.

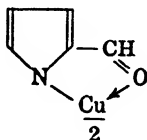
(v) **Oxime derivatives of heterocyclic nitrogen compounds.** Phenyl- α -pyridyloxime yields cyclic platinum and palladium compounds which have the following structure:



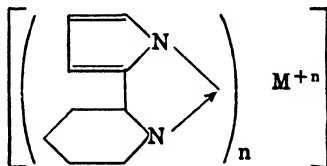
Methyl- α -pyridylketoxime reacts similarly.

(w) **Diimino compounds.** Indigo and similar compounds form metallic derivatives by replacement of the hydrogen atom of one imino group by a metal and coordination of the metal with the nitrogen atom of the second imino group. The copper derivative of indigo is an example of this type.^{70,71}

(x) **Imino carbonyl compounds.** α -Pyrrolealdehyde, prepared by the action of the aldehyde on copper oxide in xylene, is regarded as the derivative of the aldehyde.⁷²



(y) **Imino derivatives of heterocyclic nitrogen compounds.** A number of metallic derivatives of $\alpha(\alpha'$ -pyridyl)-pyrrole have been prepared.^{72,73} The pyrrole group acts as an acid in these compounds while the metal coordinates with the adjacent nitrogen atom. The cupric, zinc, cadmium, nickelous, ferric and cobaltic compounds are typical inner-complexes of the following composition:

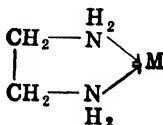


where n is 2 or 3.

Somewhat similar compounds have been prepared from aldimethylimines, such as α -pyrrolealdimethylimine.⁷²

Compounds of Type C

The third type of chelate ring is obtained with molecules capable of forming two coordinate links. Typical of these are the metallic complexes of ethylenediamine.



Rings containing 2 coordinate links are generally the least stable of the three types, since relatively stable molecules or ions are formed when the ring is broken. The most common examples of this type of structure are found in the complexes containing a powerful coordination center, such as cobalt, nickel, iridium or platinum. Both 5- and 6-membered rings are known, but available evidence indicates that 5-membered rings form more easily. Thus, with 1,2,3-triaminopropane, which is capable of forming either a 5- or 6-membered ring

with platinum chloride, apparently forms the 5-membered ring, since in this compound there is an asymmetric carbon atom while in the 6-membered ring there is none. The platinum complex has actually been resolved into two optically active forms.^{74,75}

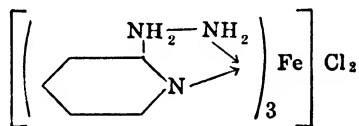
Rings of Type C containing more than 6 atoms either do not form or are extremely unstable. Rings containing 4 atoms are known. Dimeric covalent halides of the trivalent metals are thought to be of this class.

Different structures capable of yielding chelate compounds of Type C are:

(a) **Diamines.** Diamines such as ethylenediamine and trimethylenediamine form cyclic compounds by coordination of the nitrogen atoms of the two amino groups.

(b) **Compounds containing two heterocyclic nitrogen atoms.** α, α' -Dipyridyl and *o*-phenanthroline form blood-red ferrous salts in which 3 molecules of the base are attached to 1 atom of iron. These compounds have the formulas $[\text{Fe}(\text{dipy})_3]\text{X}_2$ and $[\text{Fe}(\text{o-phen})_3]\text{X}_2$. Compounds possessing similar structures and which might be expected to react similarly, such as α -pyridyl- α -quinoline and α, α' -diquinolyl fail to give the ferrous reaction.^{76,77}

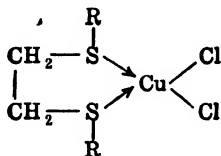
(c) **Amino derivatives of heterocyclic nitrogen compounds.** α -Pyridylhydrazine yields a ferrous complex similar to that with dipyridyl.



(d) **Dihydroxy compounds.** Compounds such as $[(\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH})_3\text{M}^{+3}]\text{X}_3$ have been reported in which the 2 oxygen atoms of the glycols form coordinate links with metals.^{78,79} Glycerol reacts similarly.⁸⁰

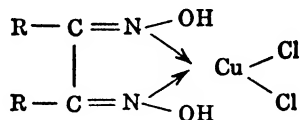
(e) **Hydroxy oximes.** Considerable evidence has been presented to show that α -benzoin oxime, which forms complexes of both Types A and B, also acts by coordination to form complexes of Type C.⁸¹ The copper complex is formed by coordination of the oxygen atom of the hydroxyl group and the nitrogen atom of the oxime group with the copper atom.

(f) **Dithioethers.** Dithioethers of the type $\text{R}-\text{S}-\text{CH}_2-\text{CH}_2-\text{S}-\text{R}$ form 5-membered rings with copper and nickel.⁸²⁻⁸⁸



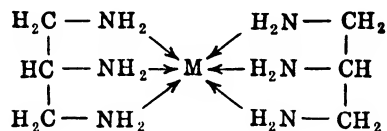
(g) **Aminothioethers.** β, β' -Diaminodiethylsulfide yields with platinum chloride a complex in which the sulfur atom and one of the amino nitrogen atoms coordinates with the platinum atom.

(h) **Dioximes.** As a rule dioximes of the 1,2-diketones form chelate rings by replacement of the hydrogen atom of one oxime group and the coordination of the nitrogen atom of the second oxime group with the metal atom. Compounds have been studied, however, in which chelate rings are formed by coordination alone.^{89,90} The copper compound is said to correspond to the following structure:



Polydentate Chelate Compounds

Organic molecules containing two coordination centers often give rise to di- and tricyclic systems. However, when 3 or more coordination centers are present, condensed chelate structures are formed. These have been called tri- and quadridentate systems. A tridentate structure is present in metallic complexes of diethylenetriamine, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$, in which the 3 amino nitrogen atoms are coordinated with the metal atom. Metals having a coordination number of 6, such as cobalt, platinum, rhodium and nickel yield complexes with 1,2,3-triaminopropane which may be represented by the following formula

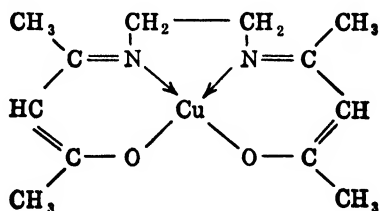


In these compounds 1 molecule of the amine occupies 3 coordination positions about the metal atom.⁹¹⁻⁹⁷

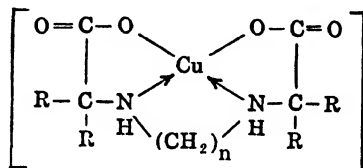
$\alpha, \alpha', \alpha''$ -terpyridyl forms a deep purple ferrous compound in which the base appears to function as a tridentate group. Platinum, rhodium and rhenium complexes have also been studied.⁹⁸⁻¹⁰⁰

A tridentate platinum compound with β, β' -diaminodiethylsulfide, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}_2$, has been prepared.¹⁰¹ The 2 amine nitrogen atoms and the sulfur atoms serve as coordination centers.

A quadridentate system is present in the complexes formed from bis-acetoacetonylethylenediamine.^{102,103}



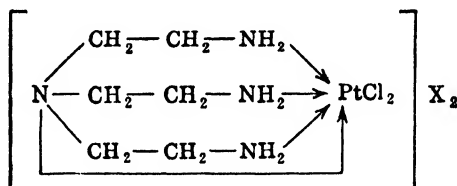
Polymethylene-bis-(α -imino acids) of the general formula $(\text{CH}_2)_n-(\text{NHCRR}'-\text{CO}_2\text{H})_2$ are reported to yield quadridentate systems.¹⁰⁴



Ethylene-bis-thioglycolic acid yields quadridentate compounds with copper and bivalent platinum.¹⁰⁵

Quadridentate structures are also formed from the phthalocyanines. The metallic complexes are produced by the action of iron or magnesium oxide on o-cyanobenzamide. These compounds bear a close structural resemblance to the porphyrins, which form the basis for many important natural pigments, such as hemaglobin and chlorophyll.

β, β', β'' -(Triaminotriethyl)amine forms quadridentate structures by 4 coordination valences.¹⁰⁶ The platinum compound is represented as follows:



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CHAPTER V

THE EFFECT OF STRUCTURE ON SOLUBILITY

THERE are few problems of analytical chemistry which are not in some way related to considerations of solubility. Methods which are based on the formation of insoluble compounds depend for their accuracy and sensitivity upon the solubility of the substance formed. The solubility of the reagents used, especially in water, is also often of critical importance. Solubility problems are of unusual interest in methods of analysis based on the use of organic reagents. The characteristic analytical reactions of organic molecules often depend on the presence of certain atomic groupings, and the remainder of the organic structure to which they are joined, or of which they form a part, is generally of secondary importance. Consequently, in many cases it is possible to prepare as reagents a series of compounds containing the same reactive grouping, but in which the remainder of the molecule is different. Because of the effect of structure and composition of organic molecules upon solubility it is often possible to improve the character of organic reagents, either through increasing their water-solubility or decreasing the solubility of the product formed in analytical reactions.

The phenomenon of solution of either a liquid or solid is a very complex process, and one that is not too well understood, but a number of generalizations have been developed which make possible a somewhat systematic study of the analytical usefulness of organic compounds from the standpoint of solubility. A few of the more important of these are discussed briefly in the following sections, which are taken largely from the work of Feigl.⁹

Relation of solubility to structure of solvent and solute. A study of the solubility of many compounds reveals that a substance is most soluble in that solvent to which it is most closely related in structure. Hexane, $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$, for example, is only sparingly soluble in water, to which it bears little structural resemblance, but is miscible in all proportions with butyl alcohol, $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{OH}$, which contains a hydrocarbon radical similar in structure to hexane. Similarly, methyl and ethyl alcohols are completely soluble in water, since alcohols, like water, contain the hydroxyl group. The lower members of the homologous series of the alkanols are closely related to water since the hydroxyl group forms a large proportion of the weight of the molecule, but the similarity becomes less with the higher members of this series, since the hydroxyl group makes up a relatively smaller part of the molecules. This difference is accompanied by a lower solubility of the higher members in water.

In general, any change in the composition or structure of a molecule which tends to make greater its similarity to water should be expected to increase its solubility in that solvent; and, conversely, any alteration in the molecule so

as to make it less like water should lead to a decreased solubility of a reaction product containing the organic structure.

Solution and solvation. The crystalline state is characterized by the fact that the structural units of a substance (atoms, ions or molecules) occupy definite positions in a crystal lattice to which they are bound by so-called *lattice forces*. These forces must be overcome during the solution of a crystal in a liquid. One source of energy for this purpose arises from the combination of the units of the lattice with molecules of the solvent. This process is generally referred to as *solvation*, or, if the solvent is water, as *hydration*. Consequently, for all crystalline solids except those of low lattice energy, solvation appears essential to solution¹; and for those compounds of low lattice energy a chemical similarity between solute and solvent appears necessary. Thus, it seems that solvation is important in the solution process, not only in providing energy for overcoming the lattice forces, but also because the formation of solvates results in an increased similarity of the solute molecules to the molecules of the solvent.

The latter idea is supported by the fact that some hydrates are more soluble in water than the corresponding anhydrous salts. For example, ferric ammonium sulfate, $\text{NH}_4[\text{Fe}(\text{SO}_4)_2]$, which differs from ferric ammonium alum only in that it has no water of hydration, is insoluble in water, whereas the alum is readily soluble. On long shaking, during which hydration probably occurs, a solution of the anhydrous compound is obtained which is identical to that of the ferric alum.² Clearly, hydration of the anhydrous compound causes an increased resemblance to water. Similarly, the anhydrous and hydrated sulfates of cobalt and nickel show significant solubility differences.

Effect of atomic groups on solubility. Although no definite relationships may be expressed between the composition of crystalline hydrates and the degree of hydration in solution, or of their solubility in water, there appears to be no doubt that the ability of a molecule to add water is an important factor in determining its water solubility. The property of hydration of an organic molecule does not appear to be a property of the molecule as a whole, but it seems rather to be localized on certain atoms or groups of atoms which form a part of the molecule. Such atoms or groups, therefore, assume a functional importance in organic reagents and also in their reaction products.

Since water is a polar solvent, its solvent action is closely related to the polar character of the solute; and the polar character of the solute molecule in turn depends on the number and character of its functional groups. All these increase the polarity although not to the same extent. Halogen atoms, ethylenic and acetylenic linkages do not affect polarity greatly, whereas the hydroxyl, carboxyl and amine groups cause a greater change in polarity.

The hydroxyl group is of great importance in enhancing the water solubility of organic compounds. For example, hydrocarbons are generally insoluble in water, whereas the corresponding alcohols and phenols are relatively more soluble. It should be noted in this connection that other factors, such as position of the hydroxyl groups, molecular weight and character of additional substituent groups also have a profound influence on solubility. The effect of

introducing hydroxyl groups into the benzene ring, and the influence of the relative positions of the groups upon the solubility of the resulting compounds is shown in Table 7.

TABLE 7.—SOLUBILITY OF PHENOLS

Compound	Solubility in g. per 100 g. of Water (20° C.)
Benzene	0.072
Phenol	9.06
1,2-Dihydroxybenzene	45.1
1,3-Dihydroxybenzene	103.0
1,4-Dihydroxybenzene	7.2
1,2,3-Trihydroxybenzene	44.4

The low solubility of the 1,4-derivative is possibly to be explained by the existence of a tautomeric quinone form.

The relative position of the hydroxyl group with respect to a group such as $=\text{CO}$, $-\text{NO}_2$, or $-\text{N}=\text{N}-$, which is capable of coordinating with the hydrogen atom of the hydroxyl group, is also important. Compounds in which the hydroxyl group is ortho to the coordinating group generally display abnormally low solubility as compared to the meta and para isomers.^{3,4} This is probably caused by the formation of a chelate ring, which is possible only with the ortho compound. Thus, with o-hydroxybenzaldehyde, a 6-membered ring is formed through coordination of the hydroxyl hydrogen atom with the oxygen atom of the carbonyl group.

The solubility of a compound in water is always decreased by replacing the oxygen atom of the molecule with a sulfur atom. Two factors appear to contribute to this result: replacement of the oxygen atom obviously reduces the similarity of the compound to water, and in addition the sulfur atom has a lower capacity for binding water than oxygen. This is illustrated by the fact that ethyl alcohol is miscible with water, whereas ethyl thioalcohol is only very slightly soluble. Similarly, phenol is fairly soluble in water although thiophenol is insoluble.

The nitrogen atom of a primary amine group is an active center for binding water molecules to organic compounds. Through hydration of amines, substituted ammonium compounds are formed, which are strongly polar and soluble in water. This effect is enhanced by replacement of the hydrogen atoms of the amine group by alkyl radicals, which increases the tendency toward hydration. The character and position of other groups in the amine molecule also have a marked influence on the solubility of the compound. If a group such as the carboxyl radical is present and so located that there is coordination between both the hydrogen atom of the carboxyl group and the nitrogen atom of the amine group, there is no possibility of hydration through coordination by either group. For example, amino acetic acid is only moderately soluble in water, whereas the ethyl ester of the acid is soluble. In the free acid there appears to

be coordination between the carboxyl hydrogen and the amine nitrogen atom, but in the ester, in which the hydrogen atom is replaced by the ethyl radical, the nitrogen atom is free to bind water molecules. This is reflected in the greater water solubility of the latter. A similar solubility relation is observed with other amino acids (in which the carboxyl group and nitrogen atom are in suitable position for coordination) and their esters. The insolubility of inner-complex salts is perhaps explained in this manner. The replacement of the hydrogen atom of the acidic group in such compounds by a metal atom, and the coordination of the metal with a nitrogen, oxygen or other atom prevents the association of water molecules, and consequently reduces the solubility of the cyclic compound in water.

The introduction of acid or basic groups often increases the solubility of organic compounds; and, as a rule, the solubility is further increased in the case of weak electrolytes by the formation of salts with acids or bases. This is particularly true for the high molecular weight carboxylic acids and bases, such as benzoic acid or α -naphthylamine. This may be explained by the fact that the ion formed by conversion of the acid or base to the salt has a greater capability of hydration than the original compound.

Influence of molecular weight on solubility. It has been shown that the water solubility of an organic molecule depends in part upon its ability to bind water molecules and thereby increase its chemical similarity to the solvent. In most cases the change is so slight as to produce no great increase in solubility, but in extreme cases the compound may become so highly hydrated that the molecule bears a close resemblance to water. In general, the hydration of compounds of high molecular weight does not produce as great a relative change in the water-like character of the compound, and consequently in its solubility in water, as in compounds of low molecular weight. Accordingly, the water solubility of the compounds of a given homologous series should decrease with increasing molecular weight. Actually, the lower members of the groups of the aliphatic alcohols and acids, for example, are miscible with water in all proportions, and the higher members are immiscible. The solubility of a few of the lower alkanols is shown in Table 8.

TABLE 8.—SOLUBILITY OF THE ALKANOLS

Alcohol	Solubility in g. in 100 g. Water 20° C.
Methyl alcohol	Miscible
Ethyl alcohol	Miscible
Propyl alcohol	Miscible
n-Butyl alcohol	8.3
n-Amyl alcohol	2.0
n-Hexyl alcohol	0.5
n-Heptyl alcohol	0.12
n-Octyl alcohol	0.03

The relationship of molecular weight and solubility is further shown in the solubility of a few amines in Table 9, and acids in Table 10.

TABLE 9.—SOLUBILITY OF AROMATIC AMINES

Amine	Solubility in Parts of Amine per 100 Parts of Water
Aniline	3.6
o-Toluidine	1.5
α -Naphthylamine	0.17

TABLE 10.—SOLUBILITY OF ACIDS

Acid	Solubility in Parts of Acid in 100 Parts of Water
Butyric acid	Miscible
Valeric acid	3.3
Caproic acid	1.1
Oenanthylic acid	0.25
Caprylic acid	0.25
Pelargonic acid	Very slightly soluble

The influence of the molecular weight on the solubility of organic compounds is an important factor in the selection of these substances for use in analytical procedures. By increasing the weight of the molecule, while still retaining the necessary functional groups, it is often possible to decrease to a considerable extent the solubility of the salts formed in precipitation reactions, and thereby to increase the sensitivity of these reactions. Further, by increasing the molecular volume it is often possible to enhance the perceptibility of reaction products. The effect of molecular weight on the solubility of salts of the aromatic sulfonic acids is shown in Table 11, which is taken from the work of Ephraim.⁵

TABLE 11.—SOLUBILITY OF METAL SULFONATES

Sulfonic Acid	Normality of Saturated Solution Salt		
	Calcium	Barium	Zinc
Benzenesulfonic acid	1.74	0.319	0.375
Naphthalene-2-sulfonic acid	0.0437	0.0069	0.0096
Anthracene-1-sulfonic acid	0.00048	0.00105	0.00086

This principle is illustrated further by the sensitivities of reactions of copper, silver and gold with thioglycolic acid, its anilide and α -naphthylamide as determined by Berg and Roebeling.⁶ These data are shown in Table 12. The tests were carried out in 0.2 N mineral acid.

TABLE 12.—SENSITIVITIES OF REACTIONS

Reagent	Sensitivity		
	Copper	Silver	Gold
Thioglycolic acid	1: 200,000	1:1,000,000	1: 500,000
Thioglycolic acid anilide	1: 4,000,000	1:3,000,000	1:1,000,000
Thioglycolic acid α -naphthylamide	1:10,000,000	1:5,000,000	1:2,500,000

Krumholz and Watzek⁷ have made similar studies on the sensitivities of reactions of salts of the complex iodobismuthous acid with homologous heterocyclic bases. The results of this study are shown in Table 13. These reactions were uniformly carried out by treating 2 drops of acid bismuth chloride solution, on a spot plate, with a drop of 0.1 alcoholic solution of the base and a drop of 1 N potassium iodide solution.

TABLE 13.—SENSITIVITY OF BISMUTH REACTIONS

Base	Mol. Wt.	Concentration Limit in 0.25 N HCl
Picoline	93	1:3,000
2-Methylbenzimidazole	132	1:10,000
Quinaldine	143	1:75,000
2-Methylbenzthiazole	149	1:75,000
β -Naphthoquinoline	193	1:500,000
2-Methyl- α (β) naphthothiazole	199	1:500,000

The dependence of reaction sensitivity upon molecular weight of the base is clearly apparent from these data.

The sensitivities of reactions with the heterocyclic bases is greatly increased by converting them into the quaternary compounds, although the effect is not to be regarded as caused solely by an increase in molecular weight. It unquestionably results at least in part from a change in the constitution of the molecule. Results of these studies indicate that solubility is not determined by the total weight of the salt, but principally by the weight and volume of the organic constituent.

Krumholz and Krumholz⁸ have shown a similar effect in the formation of double salts of zinc thiocyanate with a number of heterocyclic styryl bases.

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CHAPTER VI

HYDROCARBONS

BECAUSE of their lack of chemical activity, the hydrocarbons are not used extensively in inorganic analysis. Most of the reported uses of these compounds as analytical reagents are as solvents and wash liquids. A few such as ethylene and acetylene may be used as reducing agents, and others of the aromatic group have applications based upon the activity of the aromatic nucleus. Representative of this class is benzene, which may be used for the determination of nitrate. Hydrocarbons are also used as immiscible liquids to form zones for the accumulation of reaction products and thus to separate them from the reaction mixture.

ACETYLENE

Synonym: Ethyne



Mol. Wt. 26.04

Beil. Ref. I, 228



Use: Detection of copper. Determination of copper, gold, silver, palladium.

Acetylene is a colorless gas. When pure it has a slight and not unpleasant odor, but usually it possesses a disagreeable odor due to presence of phosphine. The gas burns with a very sooty flame. It is not explosive at ordinary pressures, but at 2 atmospheres or more it explodes violently when ignited. Since acetylene forms insoluble, explosive compounds with copper and silver, copper or brass containers must not be used for collection or storage of this gas.

Preparation: Acetylene is conveniently prepared by treating calcium carbide with water.

Separation and determination of copper. When acetylene is passed into ammoniacal, acetic acid or tartaric acid solutions containing copper salts which have previously been reduced with hydroxylamine hydrochloride, all the copper is precipitated as copper acetylide.^{1,2} The only other metals precipitated under the above conditions are silver, mercury, palladium, osmium and gold. Other metals, such as iron, aluminum and bismuth, are precipitated on the addition of ammonia, but these may be kept in solution by the addition of ammonium tartrate. Thus it will be seen that copper can be separated conveniently from most metals by reduction with acetylene.

The precipitation and determination of copper with the aid of acetylene was first used by Soderbaum³ and has since been studied by many investigators.^{2,4-11} Schreiber¹¹ reports that after precipitation of copper as the acetylide, the copper may be determined satisfactorily by any one of three different methods.

These are:

- (a) By weighing as copper thiocyanate;
- (b) By weighing as cuprous sulfide;
- (c) By weighing as copper acetylide.

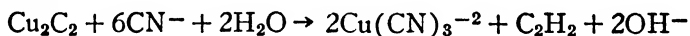
Briefly, these procedures may be carried out as follows:

(a) Determination as copper thiocyanate. Oxidize the precipitated acetylide with potassium permanganate, reduce the resulting manganese dioxide with sulfur dioxide and filter. Make the mixture alkaline with ammonium hydroxide, and then just acid with hydrochloric acid, and finally precipitate copper with ammonium thiocyanate. Filter in a Gooch crucible, wash, dry at 120-130° C., and weigh.

(b) Determination as cuprous sulfide. Filter the precipitate of the acetylide through a previously ignited Gooch crucible, and treat several times with 3 per cent ammonium sulfide. Place the crucible inside a larger crucible, mix the precipitate with sulfur, and ignite to constant weight in a current of hydrogen.

(c) Determination as copper acetylide. Spread the washed acetylide evenly and press the mass together with the flattened end of a glass rod; and wash again, first with water, then with alcohol, and finally with ether. In a double walled copper vessel, place a 1 cm. layer of calcium chloride, and on this layer place a filter paper and a filter plate, and on this place the Gooch crucible. Pass dry carbon dioxide over the crucible while drying and cooling. Drying requires about 2-2.5 hours. The average results obtained using this method are about 0.1 per cent too high. When the precipitate is dried in air, however, the results are about 0.3 per cent too high.

A fourth procedure, proposed by Iol'son^{4,5} is based upon the formation of copper acetylide, and titration of the acetylide with potassium cyanide according to the equation.



This method may be illustrated by a procedure described for determining copper in copper matte.¹²

Procedure. Dissolve 0.25 g. of the finely ground sample in 10 ml. of concentrated nitric acid, 0.3 g. of potassium chlorate, and 3 ml. of concentrated hydrochloric acid. Evaporate the resulting solution to a few ml., and add 5 ml. of concentrated sulfuric acid. Evaporate until the mixture fumes strongly. Cool, add 50 ml. of hot water, and 15 ml. of 20 per cent solution of citric or tartaric acids or 3-5 g. of sodium pyrophosphate. Next add concentrated ammonia until the solution turns blue, and then add 10 ml. in excess. Add about 0.2 g. of hydrazine sulfate or chloride to reduce the bivalent copper, and then pass acetylene through the solution for about 2 minutes to precipitate copper as copper acetylide. Titrate the mixture with approximately 1 per cent standardized potassium cyanide solution until the red precipitate dissolves completely and

the solution shows no pink coloration. The potassium cyanide solution is standardized against pure copper, using exactly the same procedure as above.

Detection of copper. Saccardi and Guiliani¹³ have used acetylene for the detection of copper in a systematic scheme of qualitative analysis. Copper is precipitated by the reagent after reduction to the cuprous state with hydroxylamine hydrochloride.

Separation and determination of palladium. Palladium is precipitated quantitatively in a hydrochloric acid solution by means of acetylene. The precipitate is reddish-brown in color, and is not constant in composition. It is filtered easily, is soluble in ammonia, potassium cyanide or an acid sulfite, and can be ignited without explosion to a lower oxide of palladium. This in turn can be reduced to the metal by ignition in a stream of hydrogen. When the palladium precipitate is washed with water, acetylene is given off slowly, but the palladium still remains in an insoluble state and consequently there is no loss from this reaction. Solid ammonium nitrate is added to the precipitate before ignition to prevent the formation of carbon from the acetylene evolved during ignition.^{14,19} The precipitation of palladium by the foregoing method appears to be satisfactory, but the precipitate is very voluminous and is therefore somewhat difficult to handle. Krauss and Deneke¹⁵ claim that it is difficult to obtain quantitative precipitation when considerable quantities of palladium are present, but they point out also that the familiar dimethylglyoxime procedure has several disadvantages.

Since palladium is precipitated by acetylene in an acid solution, and copper is precipitated from an ammoniacal solution, it is possible to obtain a good separation of copper from palladium. Palladium is first precipitated by acetylene from a hydrochloric acid solution and removed by filtration. The filtrate is then made alkaline with ammonia, the copper reduced with hydroxylamine hydrochloride, and finally precipitated by the addition of more acetylene.¹⁴ Palladium may also be quantitatively separated from platinum and iridium by precipitation with acetylene in a hydrochloric acid solution.¹⁶

Osmium is slowly precipitated by acetylene as the metal. If palladium is also present the precipitation of osmium is more rapid, and both metals can be completely precipitated in about 40 minutes. Palladium and osmium, therefore, cannot be separated by this method.

Separation and determination of gold. Gold is precipitated as the metal by passing acetylene through an acid solution of a gold salt. A similar reaction does not take place in an alkaline solution.¹⁶ Maxson¹⁷ has based a colorimetric method for determining gold upon the formation of red colloidal gold by treating a gold chloride solution with acetylene.

Separation and determination of silver. Strizhevskii¹⁸ has used acetylene for the separation and determination of silver.

Procedure. Heat to 60° C. 25 ml. of a dilute nitric acid solution containing a minimum of 0.01 g. of silver. Add 5 ml. of 50 per cent tartaric acid and 10 ml. of concentrated ammonium hydroxide. Pass acetylene (freed from

phosphine and hydrogen sulfide) through the mixture for 15 minutes. Filter, wash the silver acetylide with water which has been saturated with acetylene, and then boil the precipitate with the filter in 30 ml. of 25 per cent nitric acid. Cool the solution and titrate with standard ammonium thiocyanate by the Volhard method.

Determination of silver by this method is impossible in the presence of lead and palladium, but it is not affected by other cations.

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ANTHRACENE

$C_{14}H_{10}$

Mol. Wt 178.22

Beil. Ref. V, 657



Use: Detection of antimony and bromine.

Anthracene occurs as colorless leaflets which exhibit a blue fluorescence. It melts at 217° C. and boils at 354-5° C. The compound darkens in sunlight. It is insoluble in water, but dissolves in methyl alcohol, ethyl alcohol, benzene, chloroform, ether, carbon disulfide, carbon tetrachloride, and toluene.

Detection of bromine. Deniges has described a method for the micro-stalloscopic detection of bromine in a chloroform solution.¹

Procedure. Shake 10-20 ml. of the sample to be analyzed with 1 ml. of chloroform and allow the layers to separate. Draw off the chloroform layer into a small tube, and add 2 drops of a 1 per cent solution of anthracene in chloroform, or 0.5 mg. of powdered anthracene. If the color of the chloroform solution of bromine is a marked reddish-yellow, evaporate spontaneously 1-2 drops of the mixture on a slide, and observe the needles of dibromoanthracene under a microscope at 130 x. If the color of the chloroform solution is faint, concentrate

by evaporation, and then add anthracene as above. Chlorine forms small, white needles with anthracene.

Detection of antimony. Anthracene reacts with antimony trichloride dissolved in carbon tetrachloride to give a green coloration.²

1. G. Deniges, *Bull. trav. soc. pharm. Bordeaux* 77, 10-12 (1939); *C.A.* 33, 3717 (1939).
2. G. Gutzeit, *Helv. Chim. Acta.* 12, 713, 829 (1929).

BENZENE

C_6H_6

Mol. Wt. 78.11

Beil. Ref. V, 179

Use: Detection of bismuth, mercuric salts and nitric acid. Determination of chloride, iron, selenium and silver.

Benzene is a clear, colorless, highly inflammable liquid possessing a characteristic odor. It boils at $80.1^\circ C.$, and has a sp. gr. of 0.8787. It is insoluble in water, but is miscible with alcohol, chloroform, ether, carbon disulfide, carbon tetrachloride, glacial acetic acid and acetone.

Detection of nitric acid. Several tests for nitric acid have been based upon the formation of nitrobenzene or m-dinitrobenzene, and the subsequent identification of these compounds. One of these, proposed by Pesetz,^{1,2,3} is based upon the Janovsky reaction,⁴ in which a red-violet to permanganate-red color is produced when m-dinitrobenzene is treated with acetone and a solution of potassium hydroxide.

Procedure. To a small quantity of a solid nitrate, add 12 drops of concentrated sulfuric acid, and 2 drops of benzene, and heat on a steam bath for 3 minutes. Add 5-8 ml. of acetone and 3 ml. of 5N sodium hydroxide solution. An intense violet color appears when the sodium hydroxide solution is added in excess, and this very slowly turns to violet-red and eventually to blood-red. If the material to be tested consists of a solution of nitrate or nitric acid, neutralize with an alkali hydroxide, evaporate to dryness and proceed as above.

This test is more specific than the usual nitrate tests. Nitrites do not give a color, but if present in the test for nitrate, the sodium hydroxide solution finally becomes colorless. Chlorates interfere and must be removed by adding dropwise a 1:200 silver sulfate solution. An excess of the silver sulfate must be avoided.

Another test for nitrate, proposed by Longinescu and Pirtea,⁵ depends upon the formation of nitrobenzene by treating a little of the substance to be analyzed with benzene and concentrated sulfuric acid, reducing the nitrobenzene to aniline, and then treating the aniline with mercuric chloride to form fuchsin.

Procedure. Add 2-3 drops of benzene and 1 ml of concentrated sulfuric acid to a little of the material to be tested in a test tube. Keeping the temperature at approximately $30^\circ C.$, add a little water, and then powdered zinc in small portions. When the reaction is complete, divide the mixture into two parts and test one for aniline with calcium hypochlorite. To the second portion add a little solid mercuric chloride and evaporate to dryness under the hood.

Carefully continue to heat the mixture until a red-green color appears on sides of the tube. Cool and add a little ethyl alcohol. If nitrate was present in original unknown the solution is colored reddish violet.

A third variation of the nitrate test using benzene depends upon the formation of nitrobenzene and its subsequent detection by its characteristic odor.^{6,7}

Procedure: Add 1 ml. of benzene and a few drops of sulfuric acid to a few mg. of the material to be tested. Allow to stand for a few minutes and pour a little of this solution on to a strip of filter paper and allow the benzene to evaporate. If nitric acid was present in the original unknown, the characteristic odor of nitrobenzene can be observed. If halogens are absent it is better to make the liquid alkaline before observing the odor.

One mg. of potassium nitrate alone, or mixed with 0.1-0.2 g. of potassium nitrite, gives a definite odor of nitrobenzene. Relatively large quantities of iodide interfere and must be removed with silver or lead acetate before making the nitrate test. Bromides, chlorides, arsenious oxide, acetates, and oxalates do not interfere.

Detection of bismuth. Girard and Fourneau⁸ detected bismuth by means of the red color which is obtained when tetracetylammonium hydroxide is added to a solution of a bismuth salt containing potassium iodide. The test is made more sensitive by extracting the colored compound in benzene (see tetracetylammonium hydroxide).

Determination of selenium. Shibata⁹ recommends the use of a little benzene, toluene, or ether in the iodometric determination of selenium. By using these reagents the deposited selenium is adsorbed at the interface of the two immiscible liquids.

Detection of mercury. The test proposed by Bornet,¹⁰ which depends upon the formation of a violet precipitate with cryogenin, is made more sensitive by adding benzene to the test solution. The violet precipitate collects at the interface of the two liquids and is more readily discernible.

Determination of iron. Many important separations may be based on the conversion of ferric iron to the cupferrate, and subsequent extraction of this complex with a 1:1 mixture of ether and benzene.¹¹

Determination of silver and chloride. Benzene may be used like toluene and other organic liquids for the determination of silver and chlorides by the Volhard method. The silver chloride collects at the interface of the two liquids and need not be removed from the solution.^{12,13}

1. M. Pesetz, *J. pharm. chim.* **29**, 460-5 (1939); *C.A.* **33**, 8141 (1939).
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3. M. Pesetz, *J. pharm. chim.* **30**, 112-17 (1939); *C.A.* **33**, 9197 (1939).
4. J. V. Janovsky, *Ber.* **24**, 971 (1891).
5. G. G. Longinescu and Th. I. Pirtea, *Bull. chim. soc. romane chim.* **34**, Nos. 1-6, 3 pp. (1931); *C.A.* **27**, 45 (1933).
6. G. G. Longinescu and G. Chaborski, *Bull. acad. Roumaine* **6**, 176-8 (1922); *C.A.* **16**, 1546 (1922).

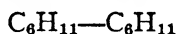
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12. M. B. Shchigol, *Z. anal. chem.* **91**, 182-5 (1932); *C.A.* **27**, 682 (1927).
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BICYCLOHEXYL

$C_{12}H_{22}$

Mol. Wt. 166.30

Beil. Ref. V, 108 (55).



Use: Determination of water.

Bicyclohexyl is a liquid boiling at 234-235° C. Its density is 0.8644.

Determination of water in alcohol. A mixture of anhydrous ethyl alcohol and bicyclohexyl has a critical solution temperature of 23.4° C. This becomes 41.4° C. with 1 per cent of water in alcohol and 54.1° with 2 per cent of water. From these data the critical solution temperature can be plotted against the per cent of water present and the resulting curve used for determining water in high proof alcohol.^{1,2}

The determination is made as follows:

Procedure. To 2.0 ml. of the alcohol add 4.0 ml. of bicyclohexyl and stir with a dry thermometer. Heat until a clear solution is obtained and then cool slowly with stirring. Note the temperature at which the well-stirred slightly opalescent mixture suddenly becomes completely turbid.

1. G. R. Robertson, *Ind. Eng. Chem., Anal. Ed.* **15**, 451-2 (1943); *C.A.* **37**, 4988 (1943).
2. G. R. Robertson, *C.A.* **37**, 6214 (1943).

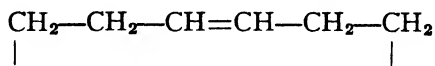
CYCLOHEXENE

Synonym: Tetrahydrobenzene

C_6H_{10}

Mol. Wt. 82.14

Beil. Ref. V, 63



Use: Detection of cyanate.

Cyclohexene is a liquid boiling at 83.3° C. Its sp. gr. is 0.810. It is very slightly soluble in water, but is soluble in alcohol and ether.

Preparation: Place 400 g. of cyclohexanol in a 500 ml. Claisen flask and add 12 ml. of concentrated sulfuric acid. Connect the flask to a condenser and receiver, which is surrounded by an ice bath. Heat the flask and contents in an

oil bath to a temperature of 130-140° C., and continue the distillation until only a small residue remains and the odor of sulfur dioxide is noticeable. Toward the end of the distillation the temperature may be raised to 150° C. Keep the receiver cold throughout the entire distillation, which requires about 5 or 6 hours. Saturate the distillation with salt and separate the cyclohexene from the aqueous layer. Dry with calcium chloride and fractionate through an efficient column. Collect the fraction boiling at 80-82° C. If necessary, fractionate the low- and high-boiling fractions once or twice to secure a pure product.¹

Detection of cyanate. If a little dry silver cyanate is suspended in ether, and the mixture treated with cyclohexene, and finally with a little iodine, 2-cyclohexylisocyanate is formed. This compound is easily recognized by its penetrating odor, or by the formation of a precipitate of 2-iodocyclohexylurea with ammonium hydroxide. Thus, after converting to the insoluble silver salt, cyanates may be detected by the above reaction.² As little as 3 mg. of potassium cyanate in 100 ml. of water can be detected by the above method, but smaller quantities do not give a precipitate with silver nitrate.

To detect cyanates in a solution of cyanide proceed as follows:²

Procedure. Dissolve 1 g. of sample in 20 ml. of water and add approximately 16 ml. of N AgNO₃ solution. Keep the mixture cool. Filter into a glass filtering crucible, and wash 3 times with each of the following: water, alcohol and ether. Dry the residue in a vacuum desiccator.

To the dry substance in a flask, add 10 ml. of ether and 1 ml. cyclohexene. Use a glass rod to produce an intimate mixture of the liquid and the silver precipitate, and then add 1 g. of iodine in small portions. Shake the mixture each time the iodine is added until the color of the iodine disappears. Approximately 30 minutes is required for addition and reaction of the iodine. Filter the mixture through paper, and into the colorless filtrate introduce ammonia gas. A white crystalline precipitate of 2-iodocyclohexylurea forms if as little as 1 per cent of potassium cyanate was present in the original sample.

By the fractional precipitation of the silver salts, using a larger sample, 0.1 per cent of potassium cyanate can be detected. The more insoluble silver cyanide forms first.

1. *Org. Synthesis*, Coll. Vol. I, 2nd ed., p. 183, John Wiley, New York (1941).

2. M. Linhard and M. Stephan, *Z. anal. Chem.* **88**, 16-23 (1932); *C.A.* **26**, 3205 (1932).

ETHYLENE

C₂H₄

Mol. Wt. 28.05

Beil. Ref. I, 180.



Use: Determination of palladium.

Ethylene is a colorless inflammable gas, which burns with a luminous flame. It possesses a suffocating, ethereal odor. One volume of the gas dissolves in

4 volumes of water at 0° C., in 9 volumes of water at 25° C., in 0.5 volume of alcohol and in 0.05 volumes of water. It is soluble in acetone and benzene.

Preparation: A steady current of ethylene gas may be obtained by the following procedure: Mix 30 ml. of ethyl alcohol and 90 ml. of concentrated sulfuric acid with 60 g. of fine sea sand in a 3-liter round-bottomed flask. Stopper the flask with a tightly fitting two-holed cork. Insert a thermometer through one of the holes so that it dips in the liquid, and through the other insert a T-tube having an internal diameter of 0.6-0.8 cm. One arm of the cross of the T is inserted in the cork so that a separatory funnel with a long stem can be inserted through the T-tube and sealed at the upper end with a short length of rubber tubing. The stem of the T serves as the outlet tube. Before the cork is pushed in the stem of the funnel, the lower end of which is constricted, it is filled by suction from a mixture of 190 ml. of alcohol and 170 ml. of concentrated acid. The mixture in the flask is heated to 160° C., and as soon as a vigorous evolution of ethylene begins, the alcohol-sulfuric acid mixture is dropped in at such rate that no copious frothing occurs and a regular current of ethylene is obtained.^{1,2}

Alcohol and ether may be removed from the gas by passing it through a wash bottle containing concentrated sulfuric acid, and sulfurous acid is removed by washing with 4 N sodium hydroxide.

Determination of palladium. When ethylene is passed through a solution containing platinum, palladium, iridium, osmium, rhodium, and ruthenium salts, palladium salts alone are reduced to the metal. Because of this selective action of ethylene in its reducing properties, palladium can accurately be determined when in the presence of other metals of the platinum group. The precipitate of metallic palladium may be filtered, dried at 105° C., and weighed.³

Procedure. Heat 10 ml. of the solution to be analyzed to 80° C. and pass ethylene gas rapidly through this solution until precipitation is complete. After about 2 hours the coagulation of the precipitate is complete and the supernatant liquid is clear and colorless. Allow the mixture to settle, filter through a Gooch crucible, wash with warm water until the washings are free of chloride, and dry in an oven at 105° C. In this way palladium may be determined with an error of only approximately 0.75 per cent.

The usual methods for reducing palladium to the metal requires ignition in a stream of hydrogen, which is a much more complicated procedure than that just described. Zinc, magnesium, formic acid, hydroxylamine, and phenylhydrazine reduce solutions of palladium chloride to the metal, but other members of the platinum group usually precipitate also. Ethylene is more suitable than carbon monoxide or acetylene for the determination of palladium. It is obtainable in compressed form, is non-toxic, and is specific in its action.

1. E. Erlenmeyer and H. Bunte, *Ann.* **168**, 64 (1873).
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3. S. C. Ogburn, Jr., and W. C. Brastow, *J. Am. Chem. Soc.* **55**, 1307-10 (1933); *C.A.* **27**, 2649 (1933).

HEPTANE C_7H_{16}

Mol. Wt. 100.20

Beil Ref. I, 154

**Use:** Determination of water.

Heptane is a hydrocarbon obtained from petroleum. It is a colorless, volatile, inflammable liquid, boiling at $98.4^\circ C.$, and having a sp. gr. of 0.684. It is insoluble in water, but is soluble in alcohol, chloroform and ether.

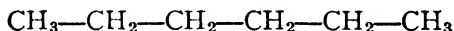
Determination of water. Water may be determined by a procedure requiring distillation with heptane.¹

1. J. J. Fox, *Oil and Color Trades J.* **91**, 993, 995 (1937); *C.A.* **31**, 8420 (1937).

HEXANE C_6H_{14}

Mol. Wt. 86.11

Beil. Ref. I, 142

**Use:** Determination of ozone.

n-Hexane is a very volatile, colorless liquid. It boils at $69^\circ C.$ and has a sp. gr. of 0.660. It is insoluble in water, but is miscible with alcohol, ether and chloroform.

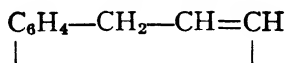
Determination of ozone. Hexane may be used as a solvent for butyraldehyde in the determination of ozone. The aldehyde is oxidized to butyric acid, which is then titrated with a standard base.¹

1. E. Briner and E. Perrottet, *Helv. Chim. Acta.* **20**, 293, 458, 1200, 1523 (1937).

INDENE C_9H_8

Mol. Wt. 116.15

Beil. Ref. V, 515

**Use:** Detection of antimony.

Indene is a liquid boiling at $181^\circ C.$

Detection of antimony. Indene reacts with antimony pentachloride in a carbon tetrachloride solution to give a bordeaux-red precipitate, which is soluble in chloroform.¹

1. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713, 829 (1929).

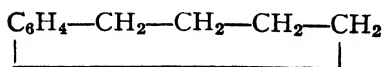
TETRALIN

Synonym: 1,2,3,4-tetrahydronaphthalene

 $C_{10}H_{12}$

Mol. Wt. 132.20

Beil. Ref. V, 491.

**Use:** Detection of manganese.

Tetralin is a water-white oil when freshly distilled, but it turns yellow and darkens with time. It boils at 207° C. and has a density of 0.9732. The compound is insoluble in water, but is miscible with benzene and acetone.

Detection of manganese. Manganese compounds react with tetralin to give a rose coloration. Lauffs^{1,2} has used this reaction as a delicate test for manganese in lithopone.

Procedure. Evaporate the lithopone under examination with a little tetralin on a water bath. A distinct pink color develops with as little as 0.005 per cent manganese.

This color change has been ascribed to the conversion of the manganese into a colloidal form of great tinting strength.

Gutzeit³ has also used this reaction for the detection of manganese in solutions of its salts.

1. A. Lauffs, *Chem.-Ztg.* 47, 315 (1923); *C.A.* 17, 2511 (1923).

2. J. V. Dubsky and A. Langer, *Chem. Obzor.* 15, 11-12 (1940); 36, 2810 (1942).

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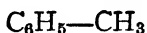
TOLUENE

Synonym: Methylbenzene, toluol

 C_7H_8

Mol. Wt. 92.13

Beil. Ref. V, 280

**Use:** Detection of mercury. Determination of chloride, selenium and water.

Toluene is a colorless refractive liquid which is obtained from coal tar. It has an odor similar to that of benzene. Its sp. gr. is 0.866 and it boils at 110.6° C. It is very slightly soluble in water but is miscible with alcohol, chloroform, ether, acetone, glacial acetic acid and carbon disulfide.

Determination of chloride. Many modifications have been proposed for the Volhard procedure for determining chlorides. This consists of precipitating the chloride with a measured excess of a standard silver nitrate solution and titrating the excess with standard thiocyanate to an end-point with ferric alum. One of the present objections to this method lies in the greater insolubility of silver thiocyanate as compared to silver chloride, and this gives rise to an error due to the conversion of some silver chloride to silver thiocyanate in the final titration. Various suggestions have been made to eliminate this difficulty. For example, the silver chloride may be removed by filtration, but this procedure entails additional effort and is not entirely accurate.

Rothmund and Burgstaller¹ have suggested shaking the silver chloride suspension with ether, chloroform or toluene to avoid filtering the precipitated silver chloride. This method has been investigated by Shchigol,² who recommends use of toluene, benzene or xylene. By covering the chloride solution with a layer of immiscible liquid, the silver chloride is drawn to the interface and thus in effect is removed from the solution. Kolthoff^{3,4} has pointed out certain disadvantages of this method.

Caldwell and Moyer⁵ have shown that the end point of the titration is partially obscured because the precipitated silver chloride turns darker more rapidly in the presence of organic liquids.

Determination of selenium. Shibata⁶ recommends the addition of benzene, toluene or ether for the iodometric determination of selenium. As in the Volhard titration, in which the silver chloride is drawn to the interface of two liquids, selenium is also removed from the solution.

Detection of mercury. A reagent prepared by mixing equal volumes of a saturated solution of iodine in ethyl alcohol and iodine in toluene reacts with mercury and mercuric sulfide to form red mercuric iodide. This reaction may be used for the detection of mercury in mercuric sulfide and for the detection of mercury metal.⁷ The insoluble residue containing mercuric sulfide, which is obtained in the usual analytical procedure, is treated with nitric acid, filtered, and washed with water. A smear of this precipitate is then placed on a strip of filter paper and treated with hydrogen sulfide for 1 or 2 minutes to transform $2 \text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$ into mercuric sulfide. The mercuric sulfide is then treated with the iodine reagent. A red color appears if mercury is present. This reaction is sensitive to 0.2 mg. of mercury. By carrying out the test on an object glass, 0.02% of mercury can be detected.

Determination of moisture. Moisture in starch, cotton and similar materials can be determined by distilling the sample with toluene or xylene and conducting the distillate into a known volume of a 1:3 mixture of acetic anhydride and pyridine. When hydrolysis is complete the excess acetic anhydride is converted into acetic acid and acetanilide, and an aliquot of the solution is titrated with standard sodium hydroxide. If X moles of acetic anhydride were used, and the sample contained Y moles of water, the acetic acid obtained in the procedure is equal to $X + Y$ moles.⁸

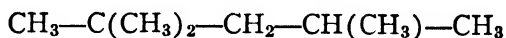
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2,2,4-TRIMETHYLPENTANE

Synonym: "Isooctane"

 C_8H_{18}

Mol. Wt. 114.22

**Use:** Determination of ozone.

2,2,4-Trimethylpentane is a colorless liquid having a density of 0.692. It boils at 99.3° C. and is insoluble in water, slightly soluble in alcohol and soluble in ether.

Determination of ozone. Briner and Perrottet^{1,2} have used the reaction between butyraldehyde and ozone as the basis for a method of determining ozone (page 374). They have found that when 2,2,4-trimethylpentane is used as the solvent for the butyraldehyde, the sensitivity of the reaction is greatly increased.¹

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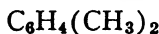
XYLENE

Synonym: Dimethylbenzene, xylol

 C_8H_{10}

Beil. Ref. 360, 361, 362, 370, 382.

Mol. Wt. 106.16

**Use:** Determination of nitrogen and water.

Commercial xylene is a mixture of the three isomers, with the m-compound predominating. It is a colorless, mobile, inflammable liquid. Its sp. gr. is approximately 0.86 and it boils between 137° and 140° C. It is insoluble in water but is miscible with absolute alcohol, ether and many other organic liquids.

Determination of nitrogen. Nitrogen in steel may be determined by an application of the method of Fue-Chan-Shi and Go-Nii-Kun.¹ The method is based on the color reaction obtained by oxidizing ammonium chloride or ammonium sulfate (formed by the decomposition of nitrogen steel in hydrochloric or sulfuric acid) with sodium hypobromite in the presence of thymol, and extracting of the coloring matter with xylene² (page 187).

Determination of water. Xylene is used in a process for the determination of water in such materials as starch or cotton. The procedure is carried out in the same manner as that described for toluene³ (page 61).

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CHAPTER VII

SUBSTITUTION PRODUCTS OF HYDROCARBONS

A few halogen and sulfur substitution products of the hydrocarbons have proved useful in analysis. These compounds are generally used as solvents. The compounds included in this chapter are:

BROMOBENZENE

Synonym: Phenyl bromide

C_6H_5Br

Mol. Wt. 157.02

Beil. Ref. V, 206 (113).

Use: Determination of copper.

Bromobenzene is a colorless refractive liquid which possesses a characteristic odor. Its sp. gr. is 1.499, and it boils at 155-56° C. It is insoluble in water, but is miscible with alcohol, benzene, chloroform and ether.

Preparation: Place 50 g. of benzene, 40 ml. of bromine and 0.5 g. of pyridine in a flask which is equipped with a vertical water condenser, and heat to 25-30° C. in a water bath. The hydrogen bromide which is evolved is led from the condenser through a tube which terminates in a funnel suspended over a beaker of water. After heating the mixture for about 1 hour, gradually increase the temperature to 65-70° C., and continue to heat at this temperature until most of the bromine has disappeared and evolution of hydrogen bromide has practically ceased. Cool the flask and contents and pour into a dilute solution of sodium hydroxide contained in a separatory funnel. Shake well. A sufficient amount of the sodium hydroxide must be present to give an alkaline reaction after shaking. Draw off the lower layer and dry over calcium chloride. When perfectly clear, filter or decant the bromobenzene into a 200-ml. distilling flask which is fitted with a thermometer, and distill over a wire gauze. After the unchanged benzene has distilled over, the temperature rises rapidly and the fraction boiling at 140-170° C. is collected separately. Redistill and collect the fraction boiling at 154-155° C.^{1,2}

Determination of copper. Ansbacher, Remington and Culp³ have used bromobenzene as a solvent for the complex copper pyridine thiocyanate which is used for the colorimetric determination of copper by Biazzo.^{4,5} Biazzo originally used chloroform to extract the copper salt, but excellent results are obtained using bromobenzene.

Procedure. Pipet an aliquot part of a neutral solution to be analyzed into a 25 ml. separatory funnel, and from a microburet, run into another separatory funnel as much standard copper sulfate solution as corresponds approximately to the copper content of the sample. To each of the funnels add approximately 10 ml. of water, 25 drops of glacial acetic acid, 30 drops of pyridine, 3 ml. of

10 per cent potassium thiocyanate solution and 2 ml. of bromobenzene (B.P. = 154-155° C.). Shake both funnels thoroughly and allow to settle, and then draw off some of the bromobenzene layer from each funnel into the corresponding cups of a colorimeter and compare. Most satisfactory results are obtained when the bromobenzene solution contains about 50-150 γ of copper.

For the details of the original Biazzo reaction, see section on pyridine.

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CARBON DISULFIDE

CS₂

Mol. Wt. 76.13

Beil. Ref. III, 197

Carbon disulfide is a colorless or faintly yellow liquid. It is very inflammable and poisonous. It has a sp. gr. of 1.272 and boils at 46.2° C. It is insoluble in water, but is miscible with anhydrous alcohol, chloroform and ether.

Carbon disulfide is an excellent solvent for many organic compounds, and most of its analytical applications are based on this property. It can be used in dithizone methods for extraction and intensification of the colored compounds formed. It may also be used to remove excess reagents when they are insoluble in water. It is also a solvent for bromine and iodine, and may be used to intensify the colors of these elements in analytical procedures. Carbon disulfide also yields colored precipitates with thallium salts and enolizable diketones (page 391).

CARBON TETRACHLORIDE

Synonym: Tetrachloromethane

CCl₄

Mol. Wt. 153.84

Beil. Ref. I, 65.

Use: Detection of boron, bromine, calcium, copper, iodine and nickel.

Determination of boron, bromine, chlorine, molybdenum, phosphorus, silver, tungsten and vanadium.

Carbon tetrachloride is a colorless, clear, non-inflammable, heavy liquid, which possesses a characteristic odor. It boils at 76.7° C. and has a sp. gr. of 1.589. It is practically insoluble in water but is miscible with alcohol, benzene, chloroform, ether and carbon disulfide.

Detection of copper and calcium. If a copper compound or an alloy of copper is placed in the flame of a Bunsen burner, the flame is colored blue when chlorine is mixed with the gas. Other elements which burn with a green flame are not affected by chlorine. Carbon tetrachloride has the same effect as chlorine and may be used much more conveniently. The test may be carried out as follows:¹

Procedure. To make test, soak a piece of cloth or cotton in carbon tetrachloride and place at the opening next the base of the Bunsen burner tube. Hold a piece of copper in the flame and observe the color.

Calcium may be detected in a similar manner, although in this case the flame turns to a reddish-orange to red. This test is more sensitive than that with copper.

Detection and determination of boron. Boric acid may be completely volatilized by heating in a current of carbon tetrachloride vapor and methyl alcohol.² Boron is completely volatilized in 1 hour at a moderate heat in a current of the vapors of 4 volumes of carbon tetrachloride and 1 volume of methyl alcohol without any decomposition.

Determination of tungsten, molybdenum, vanadium and phosphorus. Jannasch and co-workers³⁻⁹ in a series of investigations have studied the principle of decomposition of minerals by means of carbon tetrachloride vapor. They have reported that the analysis of compounds of tungsten, molybdenum and phosphorus or minerals containing these substances, is facilitated by quantitatively removing them in a stream of carbon tetrachloride.

Moser and Schmidt¹⁰ recommend the determination of tungsten compounds by distillation in a stream of carbon tetrachloride mixed with air instead of carbon dioxide. Jannasch and Harwood^{7,8,9} recommend the analysis of vanadium compounds by a procedure based on the volatility of vanadyl chloride when a vanadium compound is heated in a current of carbon tetrachloride. Carbon tetrachloride is added dropwise to sulfuric acid heated to 120-140° C. and the vapor is then conducted into a slightly heated tube containing the vanadium compound. Carbon dioxide is then passed through the tube and when all the vanadium is volatilized the residue is allowed to cool in a current of this gas. The vanadyl chloride is collected in a receiver containing 200 ml. of water and 50 ml. of nitric acid. The solution is evaporated and the vanadic acid is dissolved in dilute sulfuric acid. The vanadium is then reduced with sulfurous acid and the resulting bright blue vanadyl sulfate is titrated with potassium permanganate.

Detection of nickel. The dimethylglyoxime test for nickel may be made more sensitive by shaking the mixture with an immiscible liquid such as carbon tetrachloride; the red precipitate separates at the boundary between the two liquids.¹¹

Detection of bromine and iodine. Iodine and bromine may be detected by the color of their solutions in carbon tetrachloride. Iodine solutions are violet and bromine solutions are brown. Iodides and bromides may be detected in this way after oxidation to the free halogen. Since carbon tetrachloride is immiscible with water, small quantities of iodine and bromine can be extracted from aqueous solutions.

Determination of bromine. Bromine may be determined colorimetrically by a method which consists in liberating bromine from its salts by means of

chlorine water, dissolving the free bromine in carbon tetrachloride, and matching the resulting yellow to brown solution so obtained with a series of standard solutions similarly prepared. The following method for the analysis of natural brines has been proposed by Sweeney and Withrow.^{12,13}

Procedure. Place 100 ml. of the brine in an evaporating dish, make alkaline with sodium carbonate and evaporate to dryness. Dissolve the residue in a little water and filter into a 250 ml. volumetric flask. Make distinctly acid with sulfuric acid and dilute to the mark. Mix thoroughly and transfer a 25 ml. aliquot to a 50-ml. Nessler tube and add chlorine water until a maximum depth of color appears. Then add 10 ml. of carbon tetrachloride and shake thoroughly. Compare the resulting color of the carbon tetrachloride solution with that of a series of standards prepared in a similar manner, using known quantities of sodium bromide.

This result is only approximate. For the final determination, prepare a second set of standards containing slightly more and slightly less bromine than is indicated by the preliminary comparison. To a second 25-ml. aliquot, add chlorine water until the maximum color develops, and then add the same quantity to each of the standards. Extract the sample with 10 ml. of carbon tetrachloride, pour onto a wet filter and after the aqueous solution has drained, perforate the paper and collect the carbon tetrachloride solution in a 25-ml. Nessler tube. Compare with the set of standards.

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CHLOROFORM

Synonym: Trichloromethane

CHCl_3

Mol. Wt. 119.39

Beil. Ref. I, 61.

Use: Detection of antimony, bromine, copper, iodine, nitrate, rhenium and zinc. Determination of aluminum, beryllium, indium, iodine, iron, magnesium and molybdenum.

Chloroform is a colorless liquid which boils at 61.26° C. It has a sp. gr. of 1.4984. Its solubility in water is 10 g. per liter at 15° C., and it is soluble in alcohol, ether, acetone, benzene and carbon disulfide.

Analytical uses. Chloroform is extensively used in qualitative and quantitative analysis. In most of its applications it is used as a solvent or for the extraction of various substances, usually from aqueous solutions. Since the liquid is heavy and only slightly soluble in water, it forms a lower layer when shaken with aqueous solutions. In this way many substances which are soluble in chloroform may be extracted from aqueous solutions, either for the purpose of rendering certain tests more sensitive or for the separation of different substances.

Chloroform is used extensively to extract and concentrate the colored products formed with metallic ions in reactions with dithizone. These applications are explained in detail in the section on dithizone.

Some other analytical applications are listed in the following sections.

(a) Detection and determination of bromine and iodine. Chloroform may be substituted for carbon disulfide for the detection of small quantities of iodine and bromine. When aqueous solutions containing the free halogen are shaken with chloroform, the organic solvent assumes a brown color with bromine and a violet color with iodine. Very small quantities of iodine may be determined colorimetrically after extracting with chloroform by comparing the color of the chloroform solution with that of standards containing known quantities of iodine.¹

Chloroform may also be used for the detection of free bromine by extracting the color given by rosaniline bisulfite,² and this reaction has also been used for the detection of other halogens.^{3,4}

(b) Detection and determination of copper. Chloroform may be used for the extraction of compounds formed in the reaction of copper with pyridine and cyanate or thiocyanate ions ^{5,6,7} (section on pyridine).

(c) Detection and determination of zinc. Chloroform is used to extract the compound formed in the reaction between zinc, pyridine and thiocyanate ⁸ (section on pyridine).

(d) Determination of beryllium and aluminum. The compound $\text{BeO} \cdot 3\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2$ is soluble in chloroform. When the freshly precipitated hydroxides of beryllium and aluminum are dissolved in glacial acetic acid and evaporated with a little water, a residue is obtained which can be extracted with chloroform for the removal of beryllium. The aluminum compound does not dissolve. This makes possible the separation of beryllium and aluminum.⁹

Korenmann ¹⁰ uses chloroform in the flotation analysis of aluminum with aluminon (section on aluminon).

Aluminum may be determined in plants by dissolving the ash in hydrochloric acid and adjusting the pH to 2.5-4.5. This solution yields a precipitate with cupferron which on shaking with chloroform produces an opacity which can be measured for the determination of aluminum. Results accurate to 95 per cent can be obtained for 0.01-0.06 mg. of aluminum.¹¹

(e) Determination of iron. The iron compound formed with 8-hydroxy quinoline is soluble in chloroform, whereas the corresponding magnesium compound is not. This makes possible the separation of iron and magnesium.¹²

(f) **Determination of zirconium.** Zirconium reacts with β -nitroso- α -naphthol to yield an intense red precipitate, which dissolves in chloroform to yield a blood-red solution. This is suitable for a colorimetric comparison.¹⁸

(g) **Determination of cobalt.** Interference due to the precipitation of cobalt nitrosite in the α -nitroso- β naphthol colorimetric method for cobalt may be avoided by the use of chloroform as the solvent.¹⁴

(h) **Detection of rhenium.** If solutions containing molybdenum and rhenium are treated with ethyl xanthate, a molybdenum complex is formed which may be extracted with chloroform. In this way interference by molybdenum is eliminated in the subsequent detection of rhenium.¹⁵

(i) **Detection of antimony.** A large number of phenols give color reactions with chloroform solutions of antimony pentachloride.¹⁶

(j) **Detection and determination of molybdenum.** Chloroform may be used to extract molybdenum xanthate¹⁷ or the molybdenum complex of cupferron.¹⁸ Molybdenum may be determined colorimetrically by the red color of the xanthate, which is extracted with chloroform before the comparison.^{19,20}

(k) **Determination of indium.** Indium ions can be completely extracted from aqueous solutions of pH 3.2-4.5 by shaking with a chloroform solution of 8-hydroxyquinoline. The resulting yellow chloroform solution may be used for the colorimetric determination of small quantities of indium.²¹

(l) **Determination of nitrate.** A solution of Brucine in chloroform has been used for the colorimetric determination of small quantities of nitrate^{22,23} (section on brucine).

(m) **Determination of magnesium.** Chloroform is used in a colorimetric method for the determination of magnesium. Magnesium is first precipitated as the hydroxyquinolate, after which the precipitate is dissolved in hydrochloric acid, diluted to a definite volume, and an aliquot is buffered with sodium acetate and treated with ferric chloride. The green-black pigment which is formed is extracted with chloroform, diluted to volume with butyl alcohol, and compared with a standard in a colorimeter.²⁴

Determination of silver and chloride. Chloroform may be used as an immiscible liquid in the Volhard titration of silver or chloride²⁵ (page 60).

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CHAPTER VIII

ALCOHOLS

Since the alcohols form metallic salts by the replacement of the hydroxyl hydrogen atom by one equivalent of a metal, these compounds constitute one of the simplest representatives of the group of acidic salinogens. In general, however, the alcohols are only very slightly acidic, and consequently only a few analytical applications based on their salt-forming properties have been reported. Certain higher alcohols, such as glycerol and mannitol prevent the precipitation of hydrated oxides, carbonates and phosphates of ferric iron and other metals. According to Traube and Kuhbier^{1,2} ferric iron forms a salt with mannitol, and similar compounds are probably formed with other higher alcohols.

Weak boric acid in the presence of polyhydric alcohols, such as glycerol and mannitol, functions as a monobasic acid of such strength that it liberates carbon dioxide from carbonates, and can be titrated with phenolphthalein as an indicator. In general, the increase of the acidity of boric acid is caused only by such alcohols as contain two hydroxyl groups which are so located as to permit the formation of stable inner-complex rings.⁸ Although solid compounds of this type have been isolated,^{4,5} proof of their structure rests largely on evidence obtained from solutions.^{6,7} The extent of the increase in the acidity of boric acid by mannitol has been studied by Treadwell and Weiss,⁸ and they have shown that the ionization constant for manitol-boric acid is $6.3-8.4 \times 10^{-6}$ while the ionization constant for pure boric acid is 6×10^{-10} . Rosenheim and Weinheber⁹ have found that glycerol may be used to enhance the acidity of weak telluric acid, and Tschakirian¹⁰ showed that germanic acid forms a complex with glycerol or mannitol which functions as a strong monobasic complex acid that can be titrated with a base in the presence of phenolphthalein.¹¹ The acidity of arsenic acid is also increased by mannitol or sorbitol.¹²

The alcohols have been most frequently employed in chemical analysis as solvents and wash liquids. Many important separations have been effected with the use of alcohols and other organic liquids that are very difficult or impossible when water alone is used as the solvent. Further, the solubilities of certain salts are decreased because of changes in the activity of their ions which are brought about by the addition of alcohols. This is illustrated by the precipitation of lead sulfate and calcium sulfate by the addition of ethyl alcohol to their aqueous solutions.

The sensitivity of many color reactions, such as those based on the formation of ferric and cobalt thiocyanates, may be increased by the addition of ethyl alcohol to aqueous solutions of the reacting substances. Some alcohols which are immiscible with water have been used for the extraction of reaction products for the purpose of improving the sensitivity of the test, or for separating compounds from interfering substances.

Among the more important separations employing alcohols are those required for the analysis of the alkali and alkaline earth metals. Willard and Smith¹³ have determined the solubility of the alkali and alkaline earth perchlorates in various alcohols and other solvents, and their results are shown in Table 14.

Hopkins and Quill¹⁴ have studied the solubilities of the rare earth chlorides and nitrates in a number of alcohols and other non-aqueous solvents. Kirn and Dunlap¹⁵ have studied the solubility of the alkali chlorides and sulfates in various alcohols.

The ester-forming properties of some alcohols, especially methyl and ethyl alcohols, have been used in analytical procedures. This has been most extensively applied to the separation and determination of boron.

The reducing properties of alcohols are also used frequently in analytical procedures.

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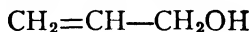
ALLYL ALCOHOL

C_3H_6O

Mol. Wt. 58.08

Beil. Ref. I, 436.

Use: Detection and determination of mercury.



Allyl alcohol is a colorless liquid, having a pungent, mustard-like odor. Its vapor is very irritating to the eyes. Its sp. gr. is 0.857 and it boils between 95.5-97° C. It is miscible with water, alcohol, chloroform and ether.

Preparation: Mix 70 g. of commercial formic acid (85 per cent) with 200 g. of glycerol in a 500-ml. flask and add a few pieces of porous plate. Attach the flask to a condenser, and insert a thermometer through the cork so that the bulb is immersed in the liquid. Heat as quickly as possible to 195° C. and collect all distillate coming over below this temperature. Change the receiver and elevate the temperature to 260° C. Collect the liquid which distills between 195-260° C. Interrupt the distillation and allow the temperature to fall to

TABLE 14.—SOLUBILITY OF PERCHLORATES IN ALCOHOLS AND OTHER ORGANIC SOLVENTS
(g. of Perchlorate per 100 ml. of Solution)

Perchlorate	Solvent								
	Water	MeOH	EtOH	n-PrOH	n-BuOH	iso-BuOH	Acetone	Ethyl Acetate	Ether
NaClO ₄	113.88	35.833	11.134	3.871	1.495	0.6264	36.596	8.425	insol
KClO ₄	2.0394	0.0830	0.0094	0.0080	0.0036	0.0040	0.1179	0.0013	insol
RbClO ₄	1.328	0.0472	0.0071	0.0048	0.0016	0.0032	0.0745	0.0014	insol
CsClO ₄	1.961	0.0734	0.0086	0.0045	0.0048	0.0056	0.1178	insol	insol
NH ₄ ClO ₄	21.91	5.268	1.488	0.3086	0.0137	0.1154	1.768	0.0268	insol
Ba(ClO ₄) ₂	128.99	119.85	78.543	52.309	41.716	36.667	81.054	80.812	insol
Ca(ClO ₄) ₂	112.34	113.68	89.551	81.690	68.419	39.567	43.812	57.377	0.185
Sr(ClO ₄) ₂	157.51	113.95	100.01	83.31	71.205	52.63	89.92	76.67	insol
Mg(ClO ₄) ₂	73.453	37.749	18.398	50.483	44.638	33.174	32.410	54.173	0.206
LiClO ₄ (anhyd.) ..	47.42	89.44	79.41	61.49	49.25	38.94	76.38	63.40	64.47
LiClO ₄ · 3H ₂ O	69.61	43.18	25.07	19.435	16.75	53.77	27.41	0.139

120-130° C., at which point an additional 50 g. of formic acid is added. Again heat rapidly to 195° C. and collect separately the fraction boiling between 195-260° C. as before. Repeat this process, and then combine the three distillates (195-260° C.). Add solid potassium carbonate, and separate the oil which collects on the surface. Extract the aqueous portion with ether, and add the ether extract to the oil. Dehydrate over potassium carbonate, remove the ether, and distill the residue (boiling point 90-95° C.).

Detection of mercury. Mercurous nitrate in dilute nitric acid solution is reduced by allyl alcohol to yield a readily observable dark-colored precipitate. This reaction is not very sensitive, but is free from interference by all common ions, including mercuric mercury. The reaction may be applied to solutions containing all common ions without previous separation of mercurous mercury.¹

Procedure. Make the solution of the mercurous salt about 3.0 N in nitric acid and add a few drops of allyl alcohol. A dark precipitate or color forms if mercurous mercury is present. The color forms more rapidly on warming if the solution is very dilute. The test is sensitive to about 0.1 mg. of mercury per ml. of solution.

Determination of mercury. Allyl alcohol reacts with a solution of a mercuric salt to form the compound $(C_3H_5O)HgX$. This compound is converted by sodium hydroxide into the base $(C_3H_5O)HgOH$. This compound does not react with phenolphthalein, but reacts with potassium iodide to form the iodide and an equivalent quantity of potassium hydroxide. Mercury can be determined indirectly by titrating the liberated potassium hydroxide with a standard acid. To make the determination, mix allyl alcohol with the sulfuric or nitric acid solution of the mercuric salt, and add a little phenolphthalein. Make alkaline with sodium hydroxide and neutralize with sulfuric acid. Finally, add potassium iodide and titrate with standard acid.^{2,3,4}

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AMYL ALCOHOL

Synonym: Isoamyl alcohol

Use: Detection of aluminum, arsenic, barium, beryllium, bismuth, calcium, cesium, chromium, cobalt, copper, iron, lithium, magnesium, molybdenum, osmium, potassium, rubidium, silver, sodium, strontium and tin. Determination of antimony, arsenic, barium, bismuth, calcium, cobalt, copper, fluorine, iron, lithium, molybdenum, osmium, sodium strontium, tin and vanadium.

The amyl alcohol originally used in chemical analysis was obtained from fusel oil, which contained 2 of the possible 8 isomers. The alcohols present in fusel oil are primary isoamyl alcohol, $(CH_3)_2CH(CH_2)_2OH$, and active amyl alcohol, $CH_3CH_2CH(CH_3)CH_2OH$. The alcohols described in the literature are not pure, and not constant in composition, but vary according to the source. The product generally used appears to be essentially primary isoamyl alcohol.

having a boiling range of 128-132° C. and a sp. gr. of 0.815-0.817.

Recently a number of synthetic amyl alcohols have been made commercially available by the Sharples Solvents Corporation. A synthetic product known as Pentasol, having a distillation range of 112-140° C., contains 5 of the 8 possible isomeric alcohols. Individual alcohols are:

Alcohol	Distillation Range ° C.	Sp. Gr.
n-Amyl alcohol (pentanol-1)	134-139	0.82
iso-Butyl carbinol (3-methylbutanol-1)	128-132	0.815
sec-Butyl carbinol (2-methylbutanol-1)	125-131	0.815
Diethyl carbinol (pentanol-3)	113-118	0.82
ter-Amyl alcohol (2-methylbutanol-2)	99-104	0.81

These alcohols are colorless liquids. They are only slightly soluble in water, but are miscible with ether and benzene.

Separation of lithium from sodium and potassium. Anhydrous lithium chloride is soluble in anhydrous amyl alcohol, whereas the chlorides of sodium and potassium are only very slightly soluble. Gooch¹⁻⁷ and others^{8,9,10} have used this difference in the solubilities of the chlorides of lithium, sodium and potassium as a basis for the separation of lithium. The quantities of the three chlorides which dissolve in 10 ml. of cold amyl alcohol are: LiCl, 0.66 g.; NaCl, 0.0003 g.; and KCl, 0.0004 g.

The following method is recommended by Gooch:

Procedure. To a concentrated solution, containing not more than 0.2 g. of lithium chloride, add 5-6 ml. of amyl alcohol (B.P. 132° C.) and carefully warm the mixture on an asbestos plate. Pass a stream of air through the liquid while boiling to prevent bumping and to facilitate the evaporation of the water. When all water has been removed, the chlorides of sodium and potassium precipitate, while nearly all of the lithium chloride remains in the alcohol. During the evaporation of the aqueous lithium chloride solution, some lithium hydroxide is formed by hydrolysis. This compound is insoluble in amyl alcohol. Convert to the chloride by adding 2-3 drops of concentrated hydrochloric acid, and then boil 2-3 minutes and filter while still warm through a small asbestos filter. Wash the residue of sodium and potassium chlorides with hot amyl alcohol which has been boiled.

Evaporate the filtrate to dryness and dissolve the residue in a little water and a little dilute sulfuric acid. Filter into a weighed platinum crucible and evaporate on a water bath. Remove the excess sulfuric acid by heating with a Bunsen burner and weigh. The lithium sulfate obtained in this manner contains small quantities of potassium and sodium sulfate if salts of these metals were originally present. To correct for these impurities deduct 0.00041 g. for each 10 ml. of the filtrate if only sodium chloride is present. Deduct 0.00051 g.

if only potassium chloride is present, and if both chlorides are present subtract 0.00092 g. The alcohol used in washing should be included in applying this correction.

If only 10-20 mg. of lithium chloride is present in the original salt mixture, the separation should be repeated.

Lithium stearate, unlike other alkali stearates, is relatively insoluble in organic solvents such as amyl alcohol. Caley¹¹ has used this property as the basis for a method of determining lithium turbidimetrically. The reagent is a saturated solution of ammonium stearate in amyl alcohol. For the details of this determination, see section on stearic acid.

Separation and detection of the alkali and alkaline earth metals. Yagoda^{12,13} has used amyl alcohol for the separation of the alkali and alkaline earth metals in a systematic procedure for the detection of these substances. This separation is based on a difference in the solubility of the bromides of these metals. These solubilities are given in Table 15.

TABLE 15.—SOLUBILITY OF ALKALI AND ALKALINE EARTH BROMIDES IN AMYL ALCOHOL AT 25° C.

(Amyl Alcohol: B.P.—129-30° C.; Sp. Gr.—0.805)

Salt	G. of Salt per ml. of Solvent
Sodium bromide	0.00085
Potassium bromide	0.000014
Lithium bromide	Very soluble
Rubidium bromide	0.00005
Cesium bromide	0.00006
Barium bromide	0.00013
Strontium bromide	0.305
Magnesium bromide	Very soluble
Calcium bromide	Very soluble

By reference to Table 15 it is noted that the bromides of sodium, potassium and barium are insoluble in amyl alcohol, whereas the bromides of calcium, strontium and magnesium are soluble. Of the less common metals, lithium accompanies the soluble group, and rubidium and cesium separate with sodium, potassium and barium bromides.

The following procedure may be used for separating the alkali and alkaline earth metals into groups as a preliminary to a systematic analysis¹²:

Procedure. Dissolve the bromides of barium, strontium, calcium, magnesium, sodium, potassium, lithium, rubidium, and cesium in the smallest possible volume of hot water and treat with 10 ml. of amyl alcohol. Evaporate to 1 ml., treat with 1 drop of 8 N hydrobromic acid and 1 ml. of isoamyl alcohol. The bromides of magnesium, strontium, calcium and lithium remain in solution, whereas the others precipitate. Filter and wash the precipitate with isoamyl alcohol containing hydrogen bromide.

Add nitric acid to the filtrate and evaporate to dryness. Add water and filter off magnesium oxide. Again evaporate to dryness with nitric acid. The strontium nitrate is practically insoluble in 1 ml. of hot concentrated nitric acid. This salt may be dissolved in 0.5 ml. of hot water and precipitated by boiling with 2 ml. of isoamyl alcohol.

The precipitate of potassium, sodium and barium bromides is treated with 95 per cent ethyl alcohol which dissolves the barium and sodium salts. After filtering, barium and sodium chlorides may be precipitated with concentrated hydrochloric acid.

Separation of potassium from sodium and calcium. Amyl alcohol is used for the determination of potassium in insoluble silicates.¹⁴ It is used for the separation of potassium from sodium and calcium. The perchlorates of sodium and calcium dissolve in amyl alcohol, while the potassium salt remains insoluble. When a mixture of the dry chlorides, containing a trace of sulfate, is extracted with amyl alcohol, the greater part of the calcium chloride dissolves, and the potassium salt is not appreciably affected.

Determination of sodium. Amyl alcohol has been used for the separation of sodium as a preliminary to the final determination of sodium in aluminum and aluminum alloys by the triple acetate method.⁵² The separation is carried out as follows:

Procedure. Place 5.0 g. of millings in a 350 ml. flask and add a few crystals of mercuric chloride. Fit the flask with a reflux condenser and add 20 ml. of amyl alcohol. Heat carefully until a vigorous reaction occurs. Remove the source of heat and add small portions of amyl alcohol until 70 ml. has been used. Boil 10 minutes until the sample is dissolved. Remove the condenser, evaporate the excess amyl alcohol, and heat until the mixture begins to fume. Cool, add 50 ml. of water, mix well and filter with suction. Evaporate the filtrate and washings to dryness, dissolve the residue in a few ml. of hot water and determine sodium as the triple acetate.

Separation and determination of barium, calcium and strontium. (a) *Separation of strontium from calcium.* Calcium nitrate is completely soluble in amyl alcohol (B.P. -128 – 130° C.), whereas strontium nitrate is practically insoluble. Browning¹⁵ has made this property the basis for a method of separating calcium and strontium.

Procedure. Dissolve about 0.5 g. of mixed nitrates of strontium and calcium in the least possible quantity of water. Boil with 30 ml. of amyl alcohol until the mixture reaches the boiling point of the alcohol indicating that all water has been expelled. Filter off the undissolved strontium nitrate through asbestos and wash with anhydrous amyl alcohol. Dissolve the residue in water and a drop of nitric acid and evaporate to dryness. Extract the residue again in the manner described above. The final determination is made by converting the calcium and strontium to the sulfates and weighing in that form.

Since strontium nitrate is not completely insoluble in amyl alcohol, add 0.001 g. of SrO for each 30 ml. of amyl alcohol used and deduct a corresponding weight from the calcium sulfate.

(b) *Separation of barium from calcium.* Barium nitrate, like strontium nitrate, is insoluble in amyl alcohol; hence, barium and calcium may be separated by a procedure exactly like that described for calcium and strontium. Since barium nitrate is more insoluble than the strontium salt no correction is needed in this separation.¹⁶

(c) *Separation of the alkali metals from calcium and magnesium.* Anhydrous hot amyl alcohol dissolves the chlorides of calcium, lithium and magnesium but not sodium and potassium. Koszegi¹⁷ states that this behavior may be used for the quantitative separation of the alkali metals from calcium and magnesium.

Separation of aluminum and beryllium. Aluminum nitrate is completely insoluble in amyl alcohol while beryllium nitrate under the same conditions is soluble. Approximately 0.1-0.13 g. of BeO dissolves in 5 ml. of amyl alcohol. Browning and Kuzirian¹⁸ have used this difference in solubility for the qualitative separation of aluminum and beryllium.

Procedure. Evaporate the aqueous solution of the mixed nitrates to a few drops and add 10-15 ml. of amyl alcohol. Heat the mixture to boiling (B.P. -128-130° C.) and continue to heat until dehydration is complete. This point is determined when the fumes burn quietly at the mouth of the test tube. Cool and filter. The precipitate is aluminum nitrate and the filtrate contains beryllium nitrate.

Detection and determination of cobalt. Amyl alcohol is used with ether for the extraction of the blue cobalt thiocyanate complex obtained in Vogel's well-known test for cobalt.¹⁹⁻²² By using a mixture of equal parts of amyl alcohol and ether 0.5 γ of cobalt may be detected.¹⁹ Pevtsov²² recommends amyl alcohol and ether mixed in the volume ratio of 2:5.

Cobalt is determined by treating a solution of a cobalt salt with ammonium thiocyanate and extracting with amyl alcohol.^{23,24,25,51} By this procedure, nickel, which produces a green color when the thiocyanate-acetone method is used, does not interfere.

Procedure. Dissolve a sample containing not more than 0.5 mg. of cobalt in 30 per cent ammonium thiocyanate solution; or, if the sample is a liquid, add solid ammonium thiocyanate in sufficient quantity to give a 30 per cent solution. Then add 0.5 g. of sodium pyrophosphate and transfer the mixture to a separatory funnel. Add 25 ml. of amyl alcohol and shake thoroughly. Separate the blue alcohol layer and transfer to a 50 ml. Nessler tube. Extract a second time, using 25 ml. of amyl alcohol, and add the second extraction to the Nessler tube. Compare the color of the alcohol extract with that of a standard prepared in a similar manner.

Danziger ²⁶ has used amyl alcohol to extract the blue color formed when ammonium thioacetate and stannous chloride are added to a solution containing cobalt. For the details of this test, see section on thioacetic acid.

Detection and determination of iron. The thiocyanate method for the detection and determination of iron depends upon the oxidation of iron to the ferric state and treating with ammonium or potassium thiocyanate. The color reaction can be made more delicate by extracting the iron compound with ether or amyl alcohol, or preferably with a mixture of 5 volumes of amyl alcohol with 2 volumes of ether.^{27-32,46} Small quantities of iron can be separated from aluminum by extracting the thiocyanate with amyl alcohol. The slightly acid solution is treated with sufficient potassium thiocyanate to make the concentration about 10 per cent, and then the mixture is extracted with about one fourth its volume of amyl alcohol until the latter no longer shows a pink color.^{47,48}

In the colorimetric determination of iron by the thiocyanate method, extraction with amyl alcohol and ether is recommended for quantities of iron less than 5 p.p.m.

Detection and determination of copper. Amyl alcohol is used to extract the copper salt of diethyldithiocarbamic acid formed in the detection and colorimetric determination of copper ^{33,34,35} (section on diethyldithiocarbamate).

Detection of chromium. Cazeneuve ³⁶ has used amyl alcohol to extract the color formed in the reaction between chromium and diphenylcarbazide. The sensitivity of the reaction is increased by this treatment (section on diphenylcarbazide).

Detection and determination of bismuth. Bismuth reacts with potassium thiocyanate to give an intense yellow color which is readily extracted from concentrated solutions by amyl alcohol.³⁷

Haddock ⁴⁹ recommends extracting bismuth in the presence of potassium iodide with a 3:1 mixture of amyl alcohol and ethyl acetate.

Bismuth may be determined colorimetrically by the formation of an orange double iodide with 8-hydroxyquinoline, and extraction with a mixture of acetone and amyl alcohol or cyclohexanol.⁵⁰

Determination of antimony. Antimony may be determined colorimetrically by extracting the yellow color formed in the reaction between tervalent antimony, pyridine, and potassium iodide. Vasil'ev and Shub ³⁸ extract the yellow color with amyl alcohol and measure the color of the alcohol solution (section on pyridine).

Determination of vanadium. Bach and Trelles ³⁹ determine vanadium colorimetrically by extracting with amyl alcohol the colored product formed in the reaction between vanadates and 8-hydroxyquinoline and comparing the color of the alcohol extract with that obtained with a standard solution of sodium vanadate similarly treated (page 297).

Procedure. Add dilute sulfuric acid to 50 ml. of a very dilute solution containing soluble vanadates until the mixture is acid to Congo red. Then add

5 drops of a solution containing 2.5 g. of 8-hydroxyquinoline in 100 ml. of a 20 per cent solution of citric acid. Shake out with 10 ml. of amyl alcohol, remove the alcohol layer, and compare colorimetrically with standard solutions containing $\text{NaVO}_3 \cdot 4\text{H}_2\text{O}$ similarly prepared.

Copper interferes with this determination but iron does not.

Detection and determination of molybdenum. Rovira⁴⁰ recommends extracting the red compound formed in the reaction between molybdenum and phenylhydrazine with amyl alcohol (section on phenylhydrazine).

Detection and determination of osmium. Amyl alcohol is used for the extraction of the color formed in the reaction between potassium thiocyanate and osmium.⁴¹

Detection of silver. Amyl alcohol intensifies the color of the compound formed in the reaction between silver and p-dimethylaminobenzalrhodanine.⁴²

Detection and determination of copper, arsenic and tin. Molybdenum in the presence of phosphoric acid may be reduced to a blue colored compound. This reaction is used for the detection of a number of reducing substances. According to Feigl,⁴³ amyl alcohol may be used as a solvent to intensify the color of the molybdenum blue reaction for the detection and determination of arsenic, copper and tin.

Determination of fluorine. Zirconium tetrachloride yields a red-violet lake with alizarin S. This is decolorized by a solution containing fluoride ion. This reaction is used for the volumetric determination of fluorides. A solution of fluoride in dilute acetic acid is added from a buret until free alizarin S is present. This is shown by the yellow color in the amyl alcohol layer which has been added to the reaction mixture.⁴⁴

Stabilization of sodium thiosulfate solution. Pregl⁴⁵ recommends adding amyl alcohol to dilute solutions of sodium thiosulfate as a stabilizing agent.

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14. C. C. Miller and F. Traves, *J. Chem. Soc.* **139**, 1390-94 (1936).
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16. P. E. Browning, *Am. J. Sci.* **43**, 314 (1892).
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- Ascorbic acid occurs in vegetables and fruits, especially in citrus fruits, and also in the leafy parts of plants. It is produced synthetically from sorbose or xylose.

The acid of commerce is about 99 per cent pure. The compound is a white, crystalline solid. It is fairly stable in air when dry, but in aqueous solution rapidly deteriorates in the presence of air. Alkalies hasten oxidation, whereas acids, hydrogen sulfide, and cyanides retard it. It is a strong reducing agent. It melts at 190-192° C. One gram of the solid dissolves in 3 ml. of water, 25 ml. of alcohol, 50 ml. of absolute alcohol, and 100 ml. of glycerol. It is insoluble in benzene, chloroform, and ether.

Determination of phosphoric acid and arsenic acid. Ammon and Hinsberg¹ and Ciocalteu² suggest that ascorbic acid can be used to advantage in place of the aminonaphtholsulfonic acid-sodium bisulfite mixture as a reducing agent in the Lohmann-Jendrassik³ method for phosphate determination. The blue color of the reduced molybdenum (phosphomolybdate) reaches its maximum in 7 minutes at 37° C. Under these conditions, the corresponding arsenomolybdate is unchanged, but reduction of this compound occurs with ascorbic acid after 15 minutes by heating the mixture to 70° C. In order to obtain satisfactory results in determining phosphate or arsenate, the reagent must be freshly prepared, the temperature carefully controlled, and a calibration curve used. The common preparation of Merck or of Hoffman-LaRoche is satisfactory.

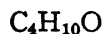
Determination of iron. Schulek and Floderer⁴ have found that ascorbic acid may be used as a reducing agent in place of sulfurous acid in a method proposed by the same authors⁵ for the colorimetric determination of iron with α,α -dipyridyl. With 0.02 g. of ascorbic acid, ferrous bipyridyl is formed within 10 minutes instead of 1 hour by the older method. This method is also recommended by Moss and Mellon.⁶

Volumetric standard. Rosenthaler⁷ reports that ascorbic acid is satisfactory as an alkalimetric and iodometric standard, but that it is unsuited for use with silver nitrate or potassium permanganate.

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n-BUTYL ALCOHOL

Synonym: Butanol-1



Mol. Wt. 74.12

Beil. Ref. I, 367.



Use: Separation and determination of lithium, potassium, ruthenium and sodium. Determination of cobalt, magnesium, phosphorus, rare earths and ruthenium.

n-Butyl alcohol is a colorless, highly refractive liquid. It has an odor similar to that of fusel oil, but weaker. Its sp. gr. is 0.810. It boils at 117-18° C. and melts at -90° C. A mixture of 63 per cent butyl alcohol and 37 per cent water forms a constant-boiling liquid, boiling at 92° C. The alcohol is soluble in about 15 parts of water, but it is miscible with alcohol or ether.

Separation and determination of sodium, potassium and lithium. A number of important separations of the alkali metals have been based on the difference in the solubility of the alkali chlorides and perchlorates in *n*-butyl alcohol and *n*-butyl alcohol mixtures. The solubility of sodium and potassium chlorides in *n*-butyl alcohol at different temperatures is shown in Table 16, which is taken from the work of Kirn and Dunlap.¹

TABLE 16.—SOLUBILITY OF ALKALI CHLORIDES IN *n*-BUTYL ALCOHOL
(Moles of Salt per Mole of Alcohol)

Temp.	NaCl	KCl
20° C.	0.0000695	0.0000822
30° C.	0.0000710	0.0000852
40° C.	0.0000762	0.0000904
50° C.	0.0000774	0.0000925

The solubilities of the chlorides and perchlorates of sodium, potassium and lithium in a number of solvents containing *n*-butyl alcohol are shown in Table 17.

TABLE 17.—SOLUBILITIES OF CHLORIDES AND PERCHLORATES
(g. of Salt per 100 g. of Solvent)

Solvent	NaCl	KCl	LiCl	NaClO ₄	KClO ₄	LiClO ₄
<i>n</i> -Butyl alcohol	0.0050	0.0030	12.98	1.83	0.0045	44.23
<i>n</i> -Butyl alcohol containing 6% HCl + 0.5% HClO ₄	0.0007	0.0005	10.61
50% <i>n</i> -butyl alcohol + 50% ethyl acetate*	11.99	0.0025

Willard and Smith² have used *n*-butyl alcohol in a procedure for the separation and determination of lithium and sodium. Sodium and lithium are first extracted from a mixture of alkali perchlorates with the alcohol, and sodium is then precipitated from the extract by means of a 20 per cent solution of hydrogen chloride in *n*-butyl alcohol. Sodium is weighed directly as the chloride and lithium is determined in the filtrate as the sulfate. This method has numerous excellent features, but is limited in scope by the fact that it has not been extended to include the separation of lithium from potassium. Later applications of this method have been used for the quantitative separation and determination of lithium, sodium and potassium. The following method may be used.³

Procedure. To about 20 ml. of solution containing the chlorides of sodium and potassium, add 5 ml. of 20 per cent perchloric acid and evaporate carefully until the salts separate. Then add 10 ml. of hot water and an additional 5 ml. of perchloric acid, and again evaporate on a water bath, and finally on a sand bath. If dense fumes of perchloric acid are not given off, repeat the addition of water and perchloric acid until fumes are obtained on evaporation. Allow to cool and add 2-3 ml. of water and warm until the solids are dissolved. To the warm solution add slowly 65-100 ml. of n-butyl alcohol containing 0.5-1.0 per cent perchloric acid. Boil 30 seconds, cool, filter, and wash with n-butyl alcohol. Dry the residue at 150-250° C. and weigh as potassium perchlorate. Sodium may be determined in the filtrate as the sulfate. The factor for potassium in potassium perchlorate is 0.2822 and for sodium in sodium sulfate 0.3238.

Lithium perchlorate, like sodium perchlorate, is soluble in n-butyl alcohol, and may be separated from potassium by the above procedure.

n-Butyl alcohol alone is not entirely satisfactory for the separation of the alkali metals because of the low solubility of sodium perchlorate, but this trouble may be eliminated by the use of a mixture of the alcohol and ethyl acetate. Sodium and lithium perchlorates are soluble in a mixture of equal parts of n-butyl alcohol and ethyl acetate, whereas potassium perchlorate is quite insoluble. Rubidium and cesium perchlorates are also insoluble in this solvent. According to Smith ⁴ a mixture of n-butyl alcohol and ethyl acetate is superior to other organic liquids for the separation of the insoluble alkali perchlorates from the soluble alkali perchlorates. The following procedure may be used in the absence of ammonium salts and sulfates:

Procedure. Dissolve the mixed alkali chlorides in a small volume of water in a Pyrex beaker, and treat with 2-3 times the equivalent quantity of 60-70 per cent perchloric acid. Do not use less than 1 ml. of the acid. Evaporate to dryness on a hot plate at a temperature not exceeding 350° C. Remove any acid from the walls of the beaker by warming with the flame of the burner. Cool, dissolve the residue in 2-3 ml. of water, and again evaporate to dryness on a hot plate. Cool and to the residue add 10-20 ml. of a mixture of equal parts of anhydrous n-butyl alcohol and ethyl acetate. The alcohol is obtained by fractionally distilling a C.P. product and collecting the fraction boiling between 116-118° C. at 760 mm. The ethyl acetate must be anhydrous and free from ethyl alcohol, and should have a purity of 99.7-100 per cent. Digest the mixture near the boiling point for 2-3 minutes and cool to room temperature. Decant the supernatant liquid through a weighed porcelain filter crucible. Wash 3 times by decantation with 3-5 ml. portions of the butyl alcohol-ethyl acetate mixture. Dissolve the residue in a minimum volume of hot water, evaporate to dryness and extract as before, using 10 ml. of the solvent. Finally transfer the residue to the filter, using a fine stream of the mixed solvent contained in a wash bottle. Wash the crucible and contents 6 times with 1 ml. portions of the mixed solvent. Dry the beaker and finally brush any particles remaining in it into the crucible. Dry the crucible at 110° C. for 10 minutes, and heat while covered at 350° C. for 15 minutes. Cool and weigh as potassium perchlorate.

The sodium, which is contained in the filtrate, may be determined by removing the ethyl acetate by evaporation, and then precipitating as sodium chloride by adding a 20 per cent solution of hydrogen chloride in butyl alcohol.⁵ Pyrex glass may be used in these separations instead of platinum.

Lithium is determined by evaporation of the n-butyl alcohol extract, and conversion of the lithium perchlorate into the sulfate in which form it is weighed.

n-Butyl alcohol may also be used for the determination of potassium in solutions containing potassium, sodium, and calcium chlorides and a little sulfate. To make this determination, precipitate the sulfate with barium chloride, add perchloric acid and evaporate to dryness. Extract the dry perchlorates of calcium, sodium and barium with an anhydrous mixture of ethyl acetate and n-butyl alcohol, and then weigh the residual potassium perchlorate.⁶

A recent procedure described by Kallmann⁷ is said to be superior to all existing methods for the separation and determination of lithium in the presence of sodium and potassium.

Procedure. Dissolved the mixed chlorides of sodium, potassium and lithium in a little water and add 5 ml. of perchloric acid. Evaporate the solution carefully to dryness on a hot plate at a temperature not exceeding 350° C. Add 20 ml. of anhydrous n-butyl alcohol and 0.2 ml. of perchloric acid and heat to boiling, and then add 8 ml. of a 20 per cent solution of hydrogen chloride in n-butyl alcohol. Add the first ml. dropwise and with constant stirring. Allow the mixture to cool to room temperature and filter through a glass filtering crucible. The precipitate, which consists of sodium chloride and a mixture of potassium chloride and perchlorate, is washed 8 times with a 6 per cent solution of hydrogen chloride in n-butyl alcohol. Retain the crucible and contents for the determination of sodium and potassium.

Dilute the filtrate and washings with one third their volume of water. Evaporate to dryness in such manner that condensation does not occur on the upper part of the beaker.

When completely dry, add 10 ml. of water, 5 ml. of nitric acid, 3 ml. of perchloric acid and 1 ml. of sulfuric acid, and evaporate on a hot plate until the sulfuric acid fumes strongly. If any brown coloration remains, add a few drops of nitric acid and again fume. Remove the excess sulfuric acid by heating, cool, and to the cool residue add 15 ml. of water. Heat the solution to boiling and transfer to a previously ignited and weighed platinum dish, and evaporate as far as possible on a water bath. Heat with a small flame of a Bunsen burner until all of the acid has been expelled, and finally heat for 1 minute at a dull red heat. Cool and weigh as lithium sulfate.

Sodium and potassium may be determined by standard methods after dissolving the residue on the filtering crucible.

Determination of cobalt. Butyl alcohol may be used to intensify the blue color of cobalt thiocyanate in the colorimetric determination of cobalt in steel.⁸

Determination of magnesium. When the precipitate obtained by treating a solution of a magnesium salt with 8-hydroxyquinoline is dissolved in

hydrochloric acid and treated with ferric chloride, a green-black compound is formed which can be extracted with chloroform, diluted with butyl alcohol and compared with standards⁹ (page 277).

Determination of rare earths. Small quantities of the rare earth elements may be isolated by extracting the thiocyanates from an aqueous solution with butyl alcohol.¹⁰

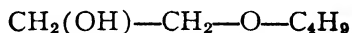
Detection and determination of ruthenium. Tervalent ruthenium reacts with an alkali thiocyanate in a dilute acid solution to give a pink color which may be extracted with n-butyl alcohol. This reaction may be used for the detection and colorimetric determination of ruthenium.

Determination of phosphorus. Phosphorus is determined colorimetrically by the Bell-Doisy method,¹¹ in which phosphorus is obtained as the yellow phosphomolybdate, and this compound is in turn converted to a blue substance by treating with a suitable reducing agent. Ether and isobutyl alcohol have been used to extract the yellow compound before the latter is reduced. Sideris¹² prefers to use n-butyl alcohol rather than ether for this extraction, although n-butyl alcohol offers no particular advantages over isobutyl alcohol for this purpose.

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8. N. Foglino and S. Bertoldi, *Ann. chim. appl.* **32**, 206-15 (1942); *C.A.* **37**, 1096 (1943).
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10. D. W. Appleton and P. W. Selwood, *J. Am. Chem. Soc.* **63**, 2029 (1941).
11. R. D. Bell and E. A. Doisy, *J. Biol. Chem.* **44**, 55 (1920).
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BUTYL CELLOSOLVE Synonym: Ethylene glycol monobutyl ether

$C_6H_{14}O_2$ Mol. Wt. 118.17



Use: Determination of iron and molybdenum.
Separation of calcium and strontium.

Butyl cellosolve is a colorless liquid, which boils at 170.6° C. It is miscible with water, and soluble in most organic solvents.

Separation of calcium and strontium. Calcium and strontium may be separated by converting to the nitrates, and then treating the nearly dry residue with butyl cellosolve. Calcium nitrate is soluble, but strontium nitrate remains undissolved.¹

Determination of iron. Rakestraw, Mahncke, and Beach² have developed a method for determining iron in sea water. This method depends on the precipitation of iron as the sulfide, solution of the sulfide in hydrochloric acid, oxidation of the iron with bromine, precipitation with ammonium hydroxide, solution of the hydrous oxide in hydrochloric acid, and determination of the iron colorimetrically as the thiocyanate. The final determination is carried out in the presence of butyl cellosolve, which is used to intensify the color. Bernhard and Dekter³ have used a mixture of ether and butyl cellosolve for the iron determination.

Determination of molybdenum. Kapron and Hehman⁴ have described a photometric method for determining molybdenum in ferrous metals in which butyl cellosolve is used to produce a stable molybdenum-thiocyanate color without the necessity of extraction with immiscible solvents. The following method for carbon and low-alloy steels illustrates this principle:

Reagents: Potassium thiocyanate solution: Dissolve 50 g. of pure potassium thiocyanate in distilled water and dilute to 1 liter.

Stannous chloride solution. Dissolve 350 g. of stannous chloride dihydrate in 250 ml. of concentrated hydrochloric acid by heating to a temperature not exceeding 50° C. Cool, add 250 ml. of water, transfer to a 1-liter flask and dilute to the mark with 1:1 hydrochloric acid. If clear, add 3-5 g. of pure tin and allow to stand 24 hours. If not clear, let stand 24 hours, filter, and add 3-5 g. of pure tin.

Procedure. Dissolve 1 g. of the sample in 5 ml. of 1:1 hydrochloric acid and 15 ml. of 70 per cent perchloric acid. If the steel contains more than 0.5 per cent carbon or 0.05 per cent sulfur, dissolve in 20 ml. of 1:1 hydrochloric acid, then add concentrated nitric acid dropwise to complete oxidation, cool slightly, and finally add 15 ml. of 70 per cent perchloric acid. Heat gently to dense fumes and continue fuming for 5-7 minutes. Cool slightly, and then immerse in cold running water. Add 20 ml. of water and boil 3-5 minutes. Cool, transfer to a 200-ml. volumetric flask, dilute to the mark with distilled water and mix thoroughly.

Transfer exactly 25 ml. of this solution to a 100-ml. volumetric flask, and add from a buret in the following order, with swirling: 15 ml. of butyl cellosolve, 5 ml. of potassium thiocyanate reagent, and 5 ml. of stannous chloride solution. Dilute to the mark with distilled water immediately after adding the stannous chloride and mix thoroughly. Let stand 10 minutes and measure the color photometrically.

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3. A. Bernhard and I. J. Dekter, *Science*, **75**, 517 (1932).
4. M. Kapron and P. L. Hehman, *Ind. Eng. Chem., Anal. Ed.* **17**, 573-6 (1945); *C.A.* **39**, 4809 (1945).

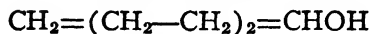
CYCLOHEXANOL

Synonym: Hexahydrophenol, hexalin

 $C_6H_{12}O$

Mol. Wt. 100.16

Beil. Ref. VI, 5.



Use: Detection and determination of bismuth molybdenum and rhenium.

Cyclohexanol consists of colorless, hygroscopic crystals, having a camphor-like odor. It melts at 20-22° C. and boils at 161° C. It is soluble in 30 parts of water.

Preparation: Cyclohexanol is prepared by the catalytic hydrogenation of phenol according to the method of Sabatier.¹

Detection and determination of molybdenum and rhenium. Cyclohexanol is used for extracting the red-colored compound formed in the reaction between molybdates and phenylhydrazine in the well-known reaction proposed by Spiegel and Mass^{2,8} (section on phenylhydrazine).

Hurd and Reynolds^{4,5} claim that cyclohexanol is a better solvent for the thiocyanate-molybdenum complex than ether or ether mixtures, so that the substitution of this solvent for ether in the colorimetric determination of molybdenum by the method of James⁶ affords greater accuracy than by the original procedure. Unlike butyl acetate, which is also superior to ether for extracting the thiocyanate-molybdenum complex, the hydrolytic products of cyclohexanol do not promote color fading.

The procedure for determining rhenium is identical to that used for molybdenum, and so cyclohexanol may be used to extract the color of the thiocyanate-rhenium complex instead of ether.

Detection and determination of bismuth. Bismuth may be detected and determined colorimetrically by the formation of the orange double iodide with 8-hydroxyquinoline and extracting with cyclohexanol.⁷

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3. L. Rovira, *Rev. facultad cienc. quim. (Univ. nacl. La Plata.)* **16**, 235-42 (1941); *C.A.* **36**, 6108 (1942).
4. L. C. Hurd and F. Reynolds, *Ind. Eng. Chem., Anal. Ed.* **6**, 477-8 (1934); *C.A.* **29**, 421 (1935).
5. L. C. Hurd, *Ind. Eng. Chem., Anal. Ed.* **8**, 11-5 (1936); *C.A.* **30**, 1325 (1936).
6. L. H. James, *Ind. Eng. Chem., Anal. Ed.* **4**, 89 (1932); *C.A.* **26**, 1211 (1932).
7. R. Sazerac and J. Fouzergues, *Compt. rend. soc. biol.* **109**, 79, 370 (1932).

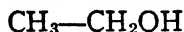
ETHYL ALCOHOL

Synonym: Ethanol

 C_2H_6O

Mol. Wt. 46.07

Beil. Ref. I, 292.



Use: Detection of bismuth, boron, cobalt, and mercury.

Determination of barium, boron, calcium, chromium, copper, iron, lead, lithium, magnesium, potassium, silver, sodium and strontium.

Ethyl alcohol is a colorless liquid boiling at 78.5° C. and having a sp. gr. of 1.7893 and a refractive index of 1.34624. It is miscible in all proportions in water, ether, acetone, methyl alcohol and chloroform.

Ethyl alcohol is one of the most widely used of all analytical solvents. It is used for the preparation of various reagent solutions, as a solvent for separating various compounds, and for the preparation of reaction media in many analytical procedures. It also appears to be indispensable for washing precipitates and equipment and for drying apparatus. It is also used as a reducing agent for such substances as manganates, permanganates, vanadium compounds, alkali ruthenates, osmium tetroxide and ceric salts. It is impossible because of the extensive bibliography to include all the references to the more general uses of alcohol in analytical procedures. Ferner and Mellon¹ have published an important review of the uses of ethyl alcohol in analytical chemistry. In the following sections a number of the more special uses of ethyl alcohol in analytical chemistry are given.

Separation and determination of potassium. Potassium may be separated from sodium by a procedure which depends upon the difference in the solubility of sodium and potassium perchlorates in alcohol. Serullas² first observed the insolubility of potassium perchlorate in ethyl alcohol and he described an analytical procedure based upon this fact. Schloessing³ appears to be the first to publish the results of analysis using this method. In this method a solution containing sodium and potassium salts was evaporated nearly to dryness with perchloric acid and the cold residue treated with strong alcohol and filtered.

Wense^{4,5} used a similar method and employed 96 per cent alcohol containing 0.2 per cent by weight perchloric acid as a wash liquid to reduce the solubility of potassium perchlorate. The perchlorate residue was extracted twice with 10 ml. of this mixture and then filtered and washed with the same liquid. The residue was finally washed with a few ml. of pure alcohol to remove the last traces of perchloric acid. Caspari⁶ has applied the perchlorate process to the determination of potassium in fertilizers, ashes and similar materials which contain iron, manganese, aluminum, phosphorus and the alkaline earths. He recommended a wash liquid containing 97 per cent alcohol and 0.2 per cent of perchloric acid; two evaporations with perchloric acid; extracting the cooled residue with 20 ml. of wash solution; decanting and repeating the extraction with an additional 20 ml. of solution; dissolving the residue in hot water and re-evaporating as suggested by Schloessing³; transferring the precipitate to a crucible with the wash fluid; and finally washing with a few ml. of pure alcohol.

The following method may be used for the separation of potassium and sodium:

Procedure. If the solution to be analyzed contains sulfate, proceed as follows: To about 70 ml. of solution containing not more than 0.5 g. of potassium salt, add 1 ml. of concentrated hydrochloric acid and heat to boiling. Add dropwise to the hot solution 0.5 N barium chloride until no further precipitation occurs. Allow the mixture to stand for 15 minutes, filter off the barium sulfate, and wash with hot water.

If ammonium salts are present, evaporate to dryness and ignite carefully until the ammonium salts are decomposed. Cool, wash the sides of the vessel with a little water and again evaporate to dryness. Finally ignite to a temperature below red heat and when cool dissolve the residue in about 20 ml. of water.

Add 5 ml. of 20 per cent perchloric acid and evaporate carefully until the salts separate. Then add 10 ml. of hot water, and an additional 5 ml. of perchloric acid and again evaporate on a water bath, and finally on a sand bath. If dense fumes of perchloric acid are not given off, repeat the addition of water and perchloric acid until fumes are obtained on evaporation. Cool to below room temperature and add 20 ml. of 97 per cent alcohol containing 0.2 per cent perchloric acid and saturated with potassium perchlorate. Break up the precipitated potassium perchlorate with a stirring rod and allow the mixture to stand for 30 minutes with the dish cooled in ice water. Filter through a Gooch crucible that has been dried at 120-130° C. and weighed. Decant the solution through the filter and wash the precipitate 3 times with small portions of alcohol containing 0.2 per cent of perchloric acid. Then dissolve the crystals in a little hot water, add 1 ml. of perchloric acid, evaporate, and treat as described above. Again transfer the pure potassium perchlorate to the weighed Gooch crucible. Wash with small portions of alcohol that has been cooled to 0° C. and saturated with potassium perchlorate and which contains 0.2 per cent perchloric acid. Dry for 1 hour at 130° C. and weigh. Factor for potassium = 0.2822.

Ammonium salts and sulfates must be absent because of the low solubility of ammonium perchlorate and sodium sulfate in alcohol. The presence of a little phosphate is not harmful since both sodium perchlorate and phosphoric acid are soluble in alcohol. Kreider⁷⁻¹⁰ used the method of Caspari⁶ and obtained good results, although the values ranged from 0.1-0.4 mg. too low. Davis¹¹ has studied the determination of potassium in fertilizers, soil extracts and plant ash by the perchlorate method and recommends that after a preliminary extraction with 20 ml. of alcohol, further washing should be carried out with a solution of potassium perchlorate in 95 per cent alcohol that is saturated at room temperature. Thin and Cumming¹² also recommend the use of a saturated solution of potassium perchlorate in 95 per cent alcohol as proposed by Davis.¹¹ They have determined the solubility of potassium perchlorate in alcohol of various strengths and in alcohol containing varying quantities of perchloric acid. Their results are shown in Tables 18 and 19.

TABLE 18.—SOLUBILITY OF POTASSIUM PERCHLORATE IN ALCOHOL AT 25.2° C.

Per Cent Alcohol (volume)	Solubility in g. of Salt per 100 g. of Solution
51.2	0.754
93.5	0.051
98.8	0.019

TABLE 19.—SOLUBILITY OF POTASSIUM PERCHLORATE IN ALCOHOL—PERCHLORIC ACID SOLUTIONS AT 25.2° C.

Solvent	Solubility in g. of Salt per 100 g. of Solution
93.5 per cent alcohol	0.051
93.5 per cent alcohol + 0.2 per cent perchloric acid ...	0.0176
98.8 per cent alcohol	0.019
98.8 per cent alcohol + 0.2 per cent perchloric acid...	0.010
98.8 per cent alcohol + 2.0 per cent perchloric acid...	0.028

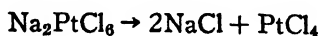
Baxter and Kobayashi^{13,14} have found that absolute alcohol, containing 0.1 per cent of perchloric acid at 0° C., dissolves potassium perchlorate to the extent of 1.9 mg. per 100 ml. They recommend washing at a temperature near 0° C. with alcohol saturated at 0° C. with potassium perchlorate. Since potassium perchlorate may be precipitated from the wash solution in the presence of much sodium, a preliminary extraction with 20 ml. of absolute alcohol containing 0.1 per cent of perchloric acid but no perchlorate is necessary before washing with the saturated perchlorate solution.^{15,16}

Morris¹⁷ has subjected the perchlorate process to a thorough investigation and makes the following recommendations:

- (a) Work at a temperature not to exceed 20° C.
- (b) Remove all ammonium compounds by preliminary treatment.
- (c) Evaporate 3 times with 20 per cent perchloric acid solution.
- (d) Dissolve the precipitate and re-evaporate if sodium is present.
- (e) Use 97 per cent alcohol containing 0.2 per cent perchloric acid as a wash liquid.
- (f) Use a minimum quantity of wash liquid.
- (g) Eliminate the final washing with pure alcohol by use of asbestos filter.
- (h) Use a Gooch crucible.
- (i) Dry at a temperature not below 130° C.

Potassium and sodium may be separated by a method which depends upon the insolubility of potassium chloroplatinate and the solubility of sodium chloroplatinate in absolute alcohol.¹⁸⁻²² Since sodium chloride is insoluble in absolute alcohol, it is necessary that both the potassium and sodium be converted to the chloroplatinate to avoid contamination of the potassium precipitate with sodium chloride.

Sodium and potassium are also separated by the use of 80 per cent ethyl alcohol. This has been recommended as superior to the stronger alcohol, since the latter possibly may lead to the decomposition of sodium chloroplatinate according to the equation



Ammonium, rubidium and cesium all yield chloroplatinates which are insoluble in alcohol and accompany the potassium if present. Ammonium salts may be

removed by ignition at low temperature. Lithium chloroplatinate is soluble and accompanies the sodium.

The solubility of potassium chloroplatinate in alcohol-water mixtures is shown in Table 20, which is taken from the work of Archibald and co-workers.⁷⁸

TABLE 20.—SOLUBILITY OF POTASSIUM CHLOROPLATINATE
IN ALCOHOL-WATER MIXTURES

Per Cent Alcohol	Grams of K_2PtCl_6 in 100 g. of Solution
100	0.0009
90	0.0025
80	0.0085
70	0.0128

The following procedure is recommended by Hillebrand ²²:

Procedure. Place about 0.2 g. or less of the chlorides of sodium and potassium in a small porcelain dish and dissolve in a little water. Add sufficient chloroplatinic acid to convert all the alkali present to the chloroplatinate. For a reagent containing 10 g. of dissolved platinum in 100 ml. of solution, use 1.7 ml. for each 0.1 g. of the chloride. Now add sufficient water to dissolve any precipitate of potassium chloroplatinate when the dish is heated on a water bath. Evaporate nearly to dryness on the water bath. The evaporation should be discontinued when the contents of the dish solidify on cooling. Wet the residue with a little 80 per cent ethyl alcohol and thoroughly stir the mass of crystals with a stirring rod. Decant the liquid through a filter moistened with alcohol and repeat the treatment of the residue with alcohol until the filtrate runs through completely colorless and the salt remaining in the dish has a pure golden-yellow color. Orange colored particles of sodium chloroplatinate must not be present. Avoid as much as possible transferring the precipitate to the filter. Dry the dish and filter to remove the alcohol, and then transfer the precipitate to a weighed crucible. Wash the dish with several small portions of hot water poured through the filter. Evaporate to dryness on a steam bath and heat in an air bath at 135° C. for 30 minutes. The crucible should be covered during the heating. Cool and weigh as potassium chloroplatinate. The potassium chloride content is obtained by multiplying the weight of the chloroplatinate by the empirical factor 0.3067.

Neubauer and Finkener ²³ have modified the chloroplatinate method so that it is not necessary that the sodium and potassium be in the form of chloride. This procedure depends upon the precipitation of the potassium chloroplatinate in the presence of an ether-alcohol mixture, igniting the precipitate in hydrogen, washing out soluble salts, and weighing as metallic platinum.

Procedure. Add a few drops of hydrochloric acid to a solution containing about 0.5 g. of mixed potassium and sodium salts in a large porcelain casserole. Add a little more than sufficient chloroplatinic acid to precipitate the

potassium, and then heat on a water bath until the volume of the solution no longer becomes smaller. Do not heat longer than necessary. Cool and add 1 ml. of water and carefully crush the crystals with the end of a flattened stirring rod. Add 30 ml. of 96 per cent alcohol in 10 ml. portions, and after each addition carefully crush the crystalline mass with a stirring rod. Cover the casserole and allow to stand for 30 minutes with frequent rubbing of the precipitate. Decant the supernatant liquid through a platinum Gooch crucible and wash the precipitate by decantation with alcohol and after each addition of alcohol crush the crystals with the rod. When the filtrate comes through colorless, transfer the precipitate to the crucible with the aid of alcohol. Wash the precipitate six times with ether to remove the alcohol and then remove the ether by drawing air rapidly through the crucible. Heat the residue in a stream of hydrogen until the chloroplatinate is converted to metallic platinum. Cool, adding a little cold water, and then draw water through the crucible 15 times to remove all of the soluble salts. Fill the crucible with 5 per cent nitric acid and allow to stand for 30 minutes with frequent replacement of fresh 5 per cent nitric acid. Finally wash with hot water, dry and weigh the platinum.

It is usually necessary to remove ammonium salts by heating before precipitating potassium with chloroplatinic acid. Because of the greater volatility of alkali chlorides, better results are obtained by igniting the sulfates. Sodium sulfate, however, is insoluble in alcohol and contaminates the precipitate of potassium chloroplatinate unless steps are included in the procedure to remove it. In a method used by Lindo and Gladding,⁷² the precipitate is washed with alcohol to remove the excess platinum, and then with a solution of ammonium chloride which is saturated with potassium chloroplatinate.

Procedure: Make the solution of alkali metals slightly acid and add 1 ml. of 18 N sulfuric acid. Evaporate to dryness and heat until ammonium salts are completely decomposed. Dissolve in a little water and precipitate potassium chloroplatinate as described above. Wash the precipitate thoroughly with 80 per cent alcohol to remove the excess chloroplatinic acid. Then wash with five 10 ml. portions of 20 per cent ammonium chloride which is saturated with potassium chloroplatinate. Again wash with 80 per cent alcohol, dry for 30 minutes and weigh.

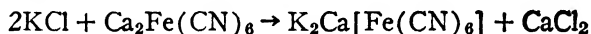
The chloroplatinate method has been used for the determination of potassium in biological materials.^{74,75}

Kunz²⁴ has devised a procedure for separating potassium from sodium by means of aniline bitartrate. The precipitant is used in an alcohol solution, and the precipitation is carried out in an alcohol solution. For the details of this procedure, see section on aniline.

Rauch²⁵ made use of the limited solubility of calcium potassium ferrocyanide in dilute alcohol in a procedure for the determination of potassium. Potassium is precipitated with a measured excess of calcium ferrocyanide and the excess titrated potentiometrically with a standard zinc sulfate solution.

Boulad²⁶ used a similar procedure for the conductometric titration of potassium.

Procedure. To a neutral solution, which is 0.015-0.06 N in potassium salt, add 36 per cent ethyl alcohol and an excess of calcium acetate. If less potassium is present use 50 per cent alcohol. Titrate with a solution of calcium ferrocyanide which is approximately 20 times as concentrated as the solution being titrated. The unknown solution should be seeded with a solution containing 0.5-1.0 g. of $K_2CaFe(CN)_6$ per 50 ml. The end point is detected by the increase in the conductance due to the excess of reagent. Calculation is based upon the following equation.



Results accurate to 1-2 per cent are claimed for this method.

Kuzirian²⁷ has used aniline perchlorate for the precipitation of potassium perchlorate in an alcoholic medium. Lutz²⁸ has used alcohol to make the silico-fluoride test more sensitive.

Determination of sodium. Alcohol is used as a medium for the precipitation of sodium as the chloride with gaseous hydrogen chloride. Potassium is previously removed as the perchlorate.^{29,30} This reaction is sensitive to 0.2 mg. Na_2O in 40 ml. of solution.

Separation of lithium from sodium and potassium. Bray³¹ has detected lithium in a systematic scheme of analysis by precipitating as the phosphate in the presence of alcohol.

Anhydrous lithium chloride is soluble in a mixture of equal parts of alcohol and ether which has been saturated with hydrogen chloride gas. Since the chlorides of sodium and potassium are practically insoluble in this mixture it may be used for the separation of lithium from potassium and sodium. This method was first proposed by Rammelsberg³² and was later recommended by Jenzsch.³³ This was later modified by Palkin³⁴ and Treadwell.³⁵ The following procedure is recommended by Treadwell:

Procedure. Evaporate the solution of the chlorides to dryness in a small flask which is so equipped that a current of dry air can be passed through it during the evaporation. When the residue is dry, place the flask on an oil bath and heat for 30 minutes at 140-150° C. while passing hydrogen chloride gas through the flask. Allow to cool while still passing hydrogen chloride through the flask. Add to the cold residue a few ml. of absolute alcohol which has been saturated with hydrogen chloride gas and then diluted with an equal volume of absolute ether. Stopper the flask tightly and allow to stand with frequent shaking for 12 hours. Filter the solution through a filter that has been moistened with the ether-alcohol mixture, and wash the residue 3 times by decantation with ether-alcohol mixture. Add a little more of the ether-alcohol mixture to the flask and again allow to stand for 12 hours. Pour off the liquid and wash the residue with ether-alcohol until a spectroscopic examination of the residue reveals no lithium. Evaporate the ether-alcohol extract to dryness on a water

bath containing lukewarm water. Moisten the residue with a few drops of dilute sulfuric acid and dissolve the mixture in the least possible quantity of water. Transfer the solution to a weighed crucible and treat with sufficient sulfuric acid to convert the lithium chloride to the sulfate. Evaporate, first on a water bath, and then cautiously over a free flame and ignite gently and weigh as lithium sulfate. The factor for lithium is 0.1263.

Winkler ³⁶ has used ethyl alcohol to extract lithium chloride from a mixture of the alkali chlorides in the determination of lithium in mineral water. Palyanichko ³⁷ has used alcohol for the separation of lithium as a preliminary to a titration of the carbonates by standard acid.

Kirn and Dunlap ³⁸ state that 1 mole of ethyl alcohol at 20° C. dissolves only 0.001147 moles of sodium chloride and 0.001270 moles of potassium chloride.

Separation of sodium, potassium and barium. After converting to the bromides, sodium, potassium and barium may be separated qualitatively as follows:

Procedure. Evaporate the solution of the bromides to dryness, and to the dried residue add 1-2 ml. of 95 per cent ethyl alcohol and 2 drops of concentrated hydrobromic acid. Heat to boiling for a time, cool and filter. The residue is largely potassium bromide. Sodium and barium may be precipitated from the filtrate by adding 0.5-1.0 ml. of 12 N hydrochloric acid. A crystalline precipitate of sodium and barium chlorides forms immediately. These metals may be identified in the usual manner.⁷¹

Determination of magnesium and calcium. Schaffgottsche ³⁹ determined magnesium by precipitating quantitatively as crystalline magnesium ammonium carbonate ($\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$) with an alcoholic solution of ammonium carbonate. This method has been modified by Gooch and Eddy ^{40,41} as follows:

Reagent. Saturate a mixture of 180 ml. of ammonium hydroxide, 800 ml. of water and 900 ml. of absolute alcohol with ammonium carbonate. Shake the mixture from time to time and filter after several hours from the excess of ammonium carbonate.

Procedure. To a neutral solution containing only magnesium and the alkali metals, preferably in the form of chlorides, add an equal volume of absolute alcohol and then an excess of the ammonium carbonate reagent. Lithium must not be present. Stir vigorously for a few minutes and allow the mixture to stand for 30 minutes. Filter through a Gooch crucible, wash with the precipitant, dry, ignite and weigh as MgO .

If large quantities of the alkali metals are present, dissolve the precipitate in hydrochloric acid, evaporate the solution to dryness, dissolve in a little water and repeat the precipitation.

Several methods have been proposed for the separation of calcium and magnesium which depend on the difference in the solubility of the sulfates in

ethyl alcohol solutions. These methods, however, do not appear to be very satisfactory.^{42,43,44} The principal sources of error are the appreciable solubility of calcium sulfate in solvents of low ethyl alcohol content, and the low solubility of magnesium sulfate in solutions having an ethyl alcohol concentration great enough to precipitate calcium sulfate quantitatively. Stolberg⁴² used a solvent consisting of 10 parts of ethyl alcohol and 90 parts of methyl alcohol. This is satisfactory but time consuming.

Travers⁴⁵ determines magnesium in hard alloys of aluminum by precipitating as magnesium ammonium phosphate. Ethyl alcohol is used to complete the separation.

Lerch and Bogue⁴⁶ have used ethyl alcohol in a procedure for the determination of uncombined lime in Portland cement. This method is based on the solution of the uncombined lime in a hot solution of glycerol and alcohol, and subsequent titration with an alcoholic solution of ammonium acetate (page 103).

Calcium and magnesium salts yield micro-crystalline precipitates with ammonium ferrocyanide in neutral solutions containing 50 per cent alcohol. The sensitivity of this reaction is about 1:1,000,000. In extreme dilutions the precipitate forms as a white turbidity and may be used for the nephelometric determination of both magnesium and calcium.⁴⁷

Separation of calcium from strontium and barium. Anhydrous calcium nitrate dissolves in a mixture of alcohol and ether, whereas barium and strontium nitrates are insoluble. This method has been used by Rose⁴⁸ and Stromeier⁴⁹ for the separation of calcium from strontium and barium.^{50,51}

Procedure. Evaporate the solution containing the nitrates of calcium, strontium and barium in a small flask which is so arranged that a stream of dry warm air passes through the flask during the evaporation. When the residue is dry, heat on an oil bath to 140° C. and keep at this temperature for 1-2 hours, while still passing the warm air through the flask. Cool, and add to the residue 10 times its weight of absolute alcohol. Stopper the flask and allow to stand, with frequent shaking, for about 2 hours. Add an equal volume of ether, close the flask and shake, and allow the mixture to stand for 12 hours. Filter through a filter moistened with the ether-alcohol mixture and wash with this mixture until a few drops of the filtrate evaporated on platinum foil leave no residue. Evaporate the filtrate to dryness on a warm water bath and dissolve the residue in water. Precipitate the calcium as the oxalate in the usual manner and after ignition weigh as the oxide. The barium may be determined as the chromate and strontium as the sulfate.

Szebelledy⁵² states that anhydrous calcium nitrate is soluble in absolute alcohol, whereas strontium nitrate is not.

Longinescu and Iordache⁵³ recommend a modified Rose procedure for the qualitative separation of calcium from barium and strontium. This consists in treating the carbonates of the metals with a mixture of 90 parts 96 per cent ethyl alcohol and 10 parts of concentrated nitric acid. Calcium nitrate passes into solution and can then be detected by means of ammonium oxalate. This method is not adaptable to quantitative procedures.

Separation of calcium and magnesium. Fresenius⁵⁴ has based a separation of calcium and magnesium upon the insolubility of calcium sulfate in alcohol:

Procedure. Evaporate a solution containing the chlorides of magnesium and calcium to dryness and dissolve the residue in strong but not absolute alcohol. Add a slight excess of concentrated sulfuric acid and allow to stand for several hours. Filter off the residue which consists of calcium sulfate and some magnesium sulfate. Wash free of acid with almost absolute alcohol and then continue the washing with 30-40 per cent alcohol ($d = 0.96$) until a few drops of the washings leave no residue on evaporation. Dry, ignite moderately and weigh as CaSO_4 . The factor for calcium oxide is 0.4119.

Chizynski⁵⁵ has used this method and claims excellent results even in the presence of phosphoric acid.

Separation of calcium and strontium. Fresenius and Ruppert⁵⁶ have separated calcium and strontium by a procedure which depends upon the differences of the solubility of their chromates in ethyl alcohol. The separation is effected by adding potassium chromate to a fairly dilute solution of the chlorides, which is free from hydrochloric acid, heating to 70°C ., and then adding a volume of alcohol equal to one third the volume of the solution. Strontium is precipitated as the chromate, although not completely. The solubility of the chromates is given in Table 21.

TABLE 21.—SOLUBILITY OF STRONTIUM AND CALCIUM CHROMATES IN WATER-ALCOHOL MIXTURES

Salt	Solubility in 29% Alcohol (by volume)	Solubility in 53% Alcohol (by volume)
SrCrO_4	0.5×10^{-4} moles per liter	1.0×10^{-4} moles per liter
CaCrO_4	7.8×10^{-3} moles per liter	5.6×10^{-2} moles per liter

Bray³¹ has used this principle for the separation of strontium in a systematic scheme of analysis.

Separation of barium from strontium and calcium. Barium silicofluoride is almost insoluble in ethyl alcohol, and this fact makes possible the separation of barium from calcium and strontium.⁵⁷

Procedure. Add an excess of fluosilicic acid to a neutral or slightly acid solution containing barium and strontium or calcium and add a quantity of alcohol ($d = 0.81$) equal to one third the volume of the solution. Allow the mixture to stand for 12 hours and collect the precipitate of barium silicofluoride on a weighed filter. Wash with a mixture of equal parts of water and alcohol until the washings no longer show the presence of even a trace of acid. The washings should not be continued longer. Dry at 110°C . and weigh. The factor for barium oxide is 0.5488.

Determination of lead. Lead may be precipitated as the sulfate in the presence of ethyl alcohol. A not too dilute solution of the lead salt is mixed with a moderately dilute solution of pure sulfuric acid in excess, and to this mixture is added a double volume of alcohol. After standing for a few hours, the mixture is filtered, the precipitate washed with alcohol, dried and ignited.

Detection of cobalt and bismuth. Because of its effect on the activities of ions, the addition of ethyl alcohol to an aqueous solution causes a shift in chemical equilibria with the formation of higher concentrations of undissociated molecules. This principle is used in increasing the sensitivity of the thiocyanate reaction for cobalt,^{58,59,60} and the iodide test for bismuth.⁶¹

In a medium containing sufficient acetone or ethyl alcohol, an alkali thiocyanate produces a blue color with cobalt, which is due to the formation of a complex cobalt thiocyanate, probably $\text{Co}(\text{SCN})_4^-$. This complex is dissociated in an aqueous solution so that no color is obtained unless the thiocyanate concentration is very large. Acetone is preferred to ethyl alcohol for color formation, since a lower concentration of the former is necessary.⁷⁶

Danziger⁶² has used alcohol in a test for cobalt with ammonium thioacetate and stannous chloride. For details of this test, see section on thioacetic acid.

Detection of mercury. Golubev⁶³ has used ethyl alcohol with toluene in the preparation of a reagent for the detection of mercury (page 61).

Determination of chromium. The violet forms of chromium sulfate and particularly the alum are insoluble in 70 per cent alcohol whereas the green forms are soluble. This fact may be used for the separation and estimation of the violet and green forms of chromium sulfate and alum.⁶⁴

Detection and determination of boron. van Giffen⁶⁵ has suggested the use of ethyl alcohol for the volatilization of boron as ethyl borate.

Determination of copper. The interference by iron with the electrolytic determination of copper can be eliminated by the addition of various organic compounds, including ethyl alcohol.⁶⁶

Determination of silver. In the deposition of silver from a nitric acid solution, alcohol is added to reduce any silver peroxide that may form during the electrolysis.⁶⁷

Determination of iron. Davidson⁷⁷ reports that when ferric hydroxide is precipitated from a boiling solution containing 50 per cent ethyl alcohol, the precipitate is granular and easy to filter and wash.

Preparation of carbonate-free sodium hydroxide. Carbonate-free sodium hydroxide may be prepared by a procedure proposed by Kuster^{68,69} which depends upon the reaction of metallic sodium with ethyl alcohol:

Procedure. Place about 40 ml. of pure ethyl alcohol in a small flask and heat to boiling on a water bath. Add in small portions 2.5 g. of bright metallic sodium, which has been freed from petroleum by rubbing with blotting paper. Keep the flask covered with a watch glass as long as the reaction is violent.

When the reaction ceases, add small quantities of carbon dioxide-free water in about 10-15 ml. portions. Boil off most of the alcohol, and finally pass a current of air, free from carbon dioxide, through the solution until the odor of alcohol can no longer be detected. Cool quickly by adding cold water, free from carbon dioxide, and immediately transfer the solution to a liter flask. Dilute to the mark with pure water.

Titration of acetic acid. Izmailov and Tartylo⁷⁰ claim that acetic acid can be titrated with aqueous hydrochloric acid with greater precision in ethyl alcohol than in water.

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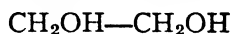
ETHYLENE GLYCOL

Synonym: Glycol



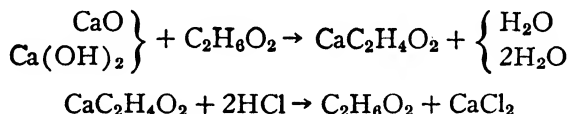
Mol. Wt. 62.07

Beil. Ref. I, 465.

**Use:** Determination of calcium oxide and calcium hydroxide.

Ethylene glycol is a colorless, syrupy liquid having a sp. gr. of 1.1176. It boils at 195-197° C. It is miscible with water and alcohol and dissolves in about 200 parts of ether.

Determination of calcium oxide and calcium hydroxide. Schlapfer and coworkers^{1,2,8,4} have used ethylene glycol for the determination of free lime and calcium hydroxide in cement clinker, cement, slag and hardened hydraulic mortar. The procedure is based on the ability of calcium oxide or calcium hydroxide to react with ethylene glycol to form soluble calcium glycolate. The latter may be titrated with standard acid. The calculations are based upon the following equations:



Procedure. Add 0.25-1.0 g. of finely powdered sample to 40-50 ml. of anhydrous glycol. This is contained in a 100 ml. round bottomed flask containing quartz grains having a diameter of about 1 mm. Stopper the flask and shake mechanically for 30 minutes at 65-70° C. Then titrate the warm mixture with 0.1 N benzoic acid in absolute alcohol to a rose-brown color with α -naphtholphthalein and phenolphthalein as indicator. The mixture may be filtered and the filtrate titrated with hydrochloric acid to an end point with methyl orange.

A modification of the above method used by MacPherson and Forbrich⁵ is satisfactory for the analysis of clinkers and Portland cements, but cannot be used for hydrated Portland cements. The determination requires only 40 minutes as compared to 1-7 hours for the glycerol-alcohol method, and is equally reliable to within 0.2 per cent.

Technical ethylene glycol containing not more than 0.5 per cent of water may be used if first neutralized by adding 0.3 g. of calcium oxide per liter and shaken for one hour at 65-70° C.

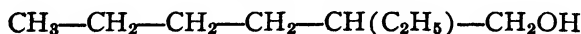
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2-ETHYLHEXANOL

Synonym: Octyl alcohol

$\text{C}_8\text{H}_{18}\text{O}$

Mol. Wt. 130.22



Use: Determination of lithium.

2-Ethylhexanol is a colorless liquid having a sp. gr. of 0.8344 and a boiling point of 184-185° C. It is soluble in 720 parts of water, and dissolves about 2.5 per cent of its weight of water at 25°.

It has not been used extensively as an analytical reagent, although several important uses have recently been suggested. Caley and Axilrod¹ claim that

this alcohol is superior to isoamyl alcohol for the separation of lithium from sodium and potassium. The solubilities of the chlorides of lithium, sodium, and potassium are given in Table 22.

TABLE 22.—SOLUBILITY OF ALKALI CHLORIDES IN 2-ETHYLHEXANOL

Alcohol	Sol. of LiCl per 100 ml.	Sol. of NaCl per 100 ml.	Sol. of KCl per 100 ml.
Octyl alcohol	3.00 g.	0.1 mg.	0.01 mg.
Isoamyl alcohol	7.30 g.	1.6 mg.	0.60 mg.

Although the solubility of lithium chloride is less in octyl alcohol than in isoamyl alcohol, the corresponding solubility of sodium and potassium chlorides is far less in octyl alcohol than in isoamyl alcohol. This makes possible a more complete separation.

Sheps and Breault² have suggested a number of uses for octyl alcohol in volumetric analysis. A 1 per cent solution of phenolphthalein in a mixture of equal quantities of ethyl alcohol and octyl alcohol can be used satisfactorily for the following operations:

(a) For determining the free alkalinity of aqueous solutions of the fatty alcohol sulfates.

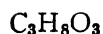
(b) For the titration in aqueous solutions of alkaline soap-like products.

(c) For the titration of acetic acid in water.

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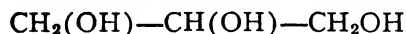
GLYCEROL

Synonym: Glycerin, trihydroxypropane



Mol. Wt. 92.09

Beil. Ref. I, 502.



Use: Detection of ammonia, boron, iron, lead, mercury and phosphate.

Determination of aluminum, boron, cadmium, calcium, copper, germanium, lead, magnesium, mercury, silicon, silver, sulfate and vanadium.

Glycerol is a colorless, clear, neutral, syrupy liquid. It possesses a sweet taste. It absorbs moist hydrogen sulfide, hydrogen cyanide and sulfur dioxide. The sp. gr. of the anhydrous compound is 1.262. It solidifies at about 0° C. and boils at approximately 290° C. with decomposition. It is miscible with water and alcohol; it dissolves in 11 parts of ethyl acetate and 500 parts of ether; but it is insoluble in benzene, chloroform, carbon disulfide and carbon tetrachloride.

Detection of boric acid. Lenher and Wells¹ have used glycerol for the detection of boric acid:

Procedure. Form a bead of potassium hydrogen sulfate and dip into a solution containing borax, and then ignite to decompose the borax and form boric acid. Cool, dip into a little glycerol and ignite. The glycerol burns with a green flame if boric acid is present. This reaction is sensitive to 0.001 g. of B_2O_3 per ml.

This reaction is much less sensitive than that employing turmeric.

When an isoalkaline solution of boric acid and of a polyhydroxy compound, which can combine with boric acid, are mixed, the pH of the resulting mixture is lower than that of the original solution. This behavior has been made the basis for a very sensitive test for boric acid by Hahn,² in which glycerol is used as the polyhydroxy compound.

Procedure. Heat a 1:1 glycerol-water mixture to boiling and add phenolphthalein, and then add 0.01 N sodium hydroxide solution until a persistent red color is obtained. Add phenolphthalein to the solution to be tested and bring to the same shade of red by the addition of 0.01 N sodium hydroxide or hydrochloric acid, whichever is required. A complete decoloration occurs when these two solutions are mixed if the unknown contained as little as 0.5 γ of boron per ml.

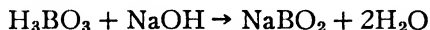
Mannitol may be substituted for glycerol (page 113).

Determination of boron. Boric acid is a very weak acid and may be titrated directly only in about normal concentration using tropeolin O or nitramine as the indicator. In titrating boric acid, however, it must be remembered that the titration exponent behaves somewhat abnormally since the dissociation constant is not a constant in the strictest sense of the word, but increases with increasing concentration because of the formation of a more highly ionized polyboric acid. Actually the direct titration of boric acid is of no great practical importance, since other and more satisfactory methods have been devised.

Boric acid reacts with polyhydric alcohols to form stronger complex acids (page 70), and these acids may be titrated with standard bases to a sharp end point with phenolphthalein. Thompson³ has recommended the addition of neutral glycerol for this purpose, and this reagent has been employed satisfactorily by many other analysts.^{4-10,40} This usage is illustrated by the following procedure proposed by Schwartz¹¹ for the determination of boron in boracite.

Procedure. Add 5-10 ml. of concentrated hydrochloric acid to 1-2 g. of finely powdered material to be analyzed and dilute to 50 or 100 ml. with water. Digest the mixture for several hours at ordinary temperature, or heat for a short time under reflux to avoid loss of volatile boric acid. Filter, wash the residue, and then make the filtrate exactly neutral to methyl orange with 0.2 N sodium hydroxide (free from carbon dioxide). Dilute to 100 or 200 ml. and then use a 25 or 50 ml. aliquot for the final titration. Mix the aliquot with the same volume of absolutely neutral glycerol, dilute somewhat, and then titrate with 0.2 N sodium hydroxide to an end point with phenolphthalein.

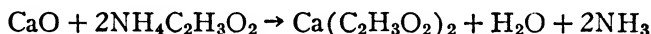
In titrating boric acid with a standard alkali in the presence of glycerol, using phenolphthalein as an indicator, the boric acid behaves as a monobasic acid according to the following reaction:



Consequently 1 ml. of N sodium hydroxide is equivalent to 0.0619 g. of H_3BO_3 .

Determination of germanium. Germanic acid, like boric acid, forms complex acids with polyhydric alcohols such as glycerol and mannitol, and these acids are much stronger than the original acids. Consequently germanic acid can be titrated with a standard base in the presence of glycerol.¹⁰

Determination of calcium. Glycerol, like ethylene glycol, reacts with the alkaline earths to yield glycerates, and this reaction has been used for the determination of calcium in cements and silicate mixtures.^{12-18,37,38} The determination is based upon the solution of uncombined lime in a hot solution of glycerol and alcohol, and the subsequent titration of the lime with alcoholic ammonium acetate in accordance with the reaction:



The following procedure, developed by Lerch and Bogue¹⁷ for the determination of uncombined lime in Portland cement, illustrates this method:

Procedure. Grind the cement to a very fine powder, and then dissolve the lime by boiling under reflux with 1 part of U.S.P. glycerol and 5 parts of absolute ethyl alcohol. The resulting solution is titrated with 0.2 N ammonium acetate in absolute alcohol containing phenolphthalein. By adding the acetate in small quantities and boiling for 20 minutes, the end point is reached when the pink color disappears and does not return on boiling. The ammonium acetate solution is standardized in a similar manner against pure calcium oxide, freshly prepared from calcium carbonate or calcium oxalate.

Diepschlag and Matting¹³ have investigated many methods for the determination of uncombined lime in slags and cement, and they have concluded that the ammonium acetate method is one of the most satisfactory procedures.

Glycerol is also used to stabilize the calcium oxalate suspension in the nephelometric determination of small quantities of calcium.³⁴

Detection and determination of mercury. Shchigol^{19,20,21} has used glycerol in a procedure which he claims is suitable for determining mercury in the presence of all cations.

Procedure. Treat the sample to be analyzed with an excess of 10 per cent potassium iodide solution and 30 per cent sodium hydroxide. Heat, and filter. To the filtrate, which contains K_2HgI_4 , add 1 ml. of glycerol and 2-3 ml. of 30 per cent sodium hydroxide solution, and then boil the mixture for several minutes. A darkening of the solution or the formation of a black precipitate occurs if mercury is present. As little as 0.25 mg. of mercury in a volume of 5-6 ml. may be detected by this procedure.

Glycerol may be used for the separation of mercury from interfering cations as a preliminary to a volumetric procedure for the determination of mercury.²²

Procedure. Dissolve 0.2-0.4 g. of sample to be analyzed in water and add 20-30 ml. of 30 per cent sodium hydroxide solution, and then add 5-10 ml. of glycerol. Boil for 5 minutes, filter, wash, and dissolve the precipitate in 15 ml. of hot nitric acid. Dilute the solution, add potassium permanganate solution until a pink color is obtained and then decolorize with ferrous sulfate solution. Finally titrate with 0.1 N ammonium thiocyanate solution.

Determination of silver. Silver is precipitated by adding glycerol to a hot alkaline and ammoniacal solution of a silver salt. Precipitation occurs with this treatment at dilutions at which a precipitate of silver chloride is not obtained. Donath²³ has used this reaction for the determination of small quantities of silver in the presence of lead.

Procedure. To a solution of lead and silver ions in dilute nitric acid, add 4-5 ml. of pure glycerol, dilute to 60 ml., and add an excess of ammonium hydroxide and 10-15 ml. of concentrated sodium hydroxide solution. A perfectly clear solution should result. Now boil for 6 minutes with frequent stirring and filter. Finally, wash the precipitate and weigh as metallic silver.

This procedure may be used in the presence of copper, since cupric hydroxide does not precipitate under the conditions of the determination.

Silver may be determined colorimetrically in a method based on the formation of a colored colloidal solution when glycerol is added to a solution of silver salt containing sodium hydroxide. As little as 0.002 mg. of silver may be detected in 50 ml. of solution. Ammonia must be absent, but copper, zinc, mercury, bismuth, cadmium and lead do not interfere unless present in such quantity as to give a precipitate with sodium hydroxide.²⁹⁻³²

Detection of iron. Iron may be detected by the yellow color which is formed when glycerol is added to a very dilute solution of a ferric salt.³³

Determination of vanadium. The salts of tetravalent vanadium liberate equivalent quantities of acid when treated with glycerol. By determining the amount of free acid, vanadium can be determined indirectly.²⁴

Detection of ammonia. Ammonia may be detected microchemically by directing the gas onto the surface of a saturated solution of picric acid in ethyl alcohol containing 5 per cent glycerol. Characteristic yellow crystals of ammonium picrate are formed.²⁶

Determination of lead and cadmium. Lead and cadmium may be determined colorimetrically after depositing electrolytically by dissolving the deposits in acid and treating with sodium sulfide and glycerol. The color of the colloidal sulfides is measured.⁴¹

Determination of copper. Interference of iron with the electrolytic determination of copper may be eliminated by the addition of glycerol.²⁵

Determination of magnesium. Thrun³⁹ has used glycerol for the preparation of starch glycerite, which is used to stabilize the lake formed in the reaction with turmeric for the colorimetric determination of magnesium.

Determination of aluminum. When the sodium salt of alizarin sulfonic acid is added to a faintly acid solution of an aluminum salt, a red coloration or precipitate is produced.³⁵ In the presence of glycerol the formation of the precipitate is retarded and the resulting colored solution may be used for the colorimetric determination of small quantities of aluminum.³⁶

Detection of phosphate. The sensitivity of the phosphomolybdate reaction for the detection of phosphorus is increased by the use of a glycerol-gelatin solution which has been boiled until the protein no longer gives a turbidity with ammonium molybdate. The following procedure may be used.²⁷

Reagent. Dissolve 5 g. of ammonium molybdate in 100 ml. of water and 35 ml. of 1:1 nitric acid.

Procedure. Boil 5 g. of phosphate-free, inert gelatin in 100 ml. of glycerol until foaming ceases and dilute 1 ml. of this solution with 10 ml. of water. Then mix with 1 ml. of the ammonium molybdate solution and add the solution to be tested. A yellow turbidity is obtained in the presence of very small quantities of phosphate.

Determination of silica. Nikola'ev⁴² has used glycerol in a procedure for the determination of silica in aluminum alloys. The washed silica precipitate is mixed with diluted glycerol until no more fine particles are observed, and the mixture is then compared under reflected light with solutions of known silica content.

Determination of sulfate. Von Stein⁴³ suggests the following method for the determination of sulfate in nickel nitrate:

Procedure. Dissolve 14.6 g. of the sample in 100 ml. of water, add 5 ml. of glycerol and 20 ml. of a 20 per cent barium chloride solution which is 0.6 N in hydrochloric acid. Allow to stand for exactly 3 minutes and measure the turbidity by interposing the solution between a 15-w. electric lamp and a photoelectric light meter. Compare with standards.

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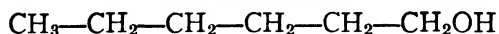
n-HEXYL ALCOHOL

Synonym: Hexanol-1

 $C_6H_{14}O$

Mol. Wt. 102.17

Beil. Ref. I, 407.

**Use:** Separation of lithium from sodium and potassium.

n-Hexyl alcohol is a colorless liquid. It has a sp. gr. of 0.820 and boils at 155-158° C. It is only slightly soluble in water but is soluble in alcohol and ether.

Separation and determination of lithium. Caley and Axilrod¹ recommend the use of n-hexyl alcohol as superior to amyl alcohol in the well-known Gooch method (page 74) for the separation of lithium from sodium and potassium. This method is based on the extraction of the mixed chlorides with

amyl alcohol. This method has the disadvantage that neither sodium nor potassium chloride is quantitatively insoluble in amyl alcohol. A comparison of the solubilities of the alkali chlorides in isoamyl alcohol and n-hexyl alcohol (Table 23) reveals the smaller solubility of sodium and potassium chlorides in the latter solvent.

TABLE 23.—SOLUBILITY OF ALKALI CHLORIDES

(g. of Salt per 100 ml. of Solvent at 20° C.)

Salt	Isoamyl Alcohol	n-Hexyl Alcohol
LiCl	7.3	5.8
NaCl	0.0016	0.0008
KCl	0.0006	0.00004

The results of separations with n-hexyl alcohol are fairly satisfactory, although results for sodium are slightly low and those for potassium slightly less so. When both sodium and potassium are present, values for lithium are slightly high. These uncorrected results, however, are much better than can be obtained with the use of isoamyl alcohol without applying solubility corrections. The alcohol is used in much the same manner as described for the amyl alcohol.

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ISOBUTYL ALCOHOL

Synonym: Isopropyl carbinol, fermentation butyl alcohol

$C_4H_{10}O$

Mol. Wt. 74.12

Beil. Ref. I, 373.



Use: Determination of barium, calcium, chlorine, lithium, phosphorus, potassium, silver, sodium and strontium.

Isobutyl alcohol is a colorless refractive liquid. It is inflammable and possesses an odor similar to, although weaker than, amyl alcohol. It boils at 106-108° C. and has a sp. gr. of 0.806. It is soluble in about 20 parts of water and is miscible with alcohol and ether.

Separation of sodium and potassium. Szebelledy and Schick¹ have proposed a method for the separation of sodium and potassium which is based upon the fact that sodium iodide is soluble in a mixture of isobutyl alcohol and ether, whereas the potassium salt is fairly insoluble. Ten ml. of a mixture of equal parts of isobutyl alcohol and absolute ether dissolve only 2 mg. of dry potassium iodide, whereas 500 mg. of sodium iodide will dissolve in the same volume of this solvent. If allowance is made for the solubility of potassium iodide, results obtained for both sodium and potassium are reported as satisfactory.

Hegedus² has employed a procedure similar to that proposed by Szebelledy and Schick¹:

Procedure. Mix sodium chloride and potassium chloride with hydrogen iodide and evaporate to dryness on a water bath. If the residue appears somewhat yellow, due to the presence of a little iodine in the iodide, moisten the residue with a little ethyl alcohol and again evaporate. Dry at 120-130° C. and after 20-30 minutes transfer to a desiccator containing sulfuric acid. Now prepare a mixture of 1 part of isobutyl alcohol and 1.5 parts of ether and saturate with potassium iodide which has been previously dried at 125° C. and ground to a powder. Determine the potassium iodide content of the solvent solution by adding chlorine and titrating the liberated iodine with sodium thiosulfate. Extract the dry mixture of potassium iodide and sodium iodide 3 times with 10 ml. portions of the isobutyl alcohol-ether mixture, and then determine the sodium iodide content of the extract plus the potassium iodide content of the residue by titrating with sodium thiosulfate after a preliminary treatment with chlorine. By correcting for the potassium iodide added to the solvent, excellent results can be obtained in determining potassium in the presence of sodium.

Separation and determination of lithium. Winkler³ has proposed separating lithium from sodium and potassium by extracting the anhydrous chlorides with isobutyl alcohol. This method is recommended by Moser and Schutt,⁴ who claim that if the chlorides are absolutely anhydrous a good separation can be obtained. For the separation, the anhydrous chlorides are extracted three times with 10 ml. portions of isobutyl alcohol. The residual chlorides are dissolved and dehydrated between extractions. Then by igniting with 3 parts of ammonium chloride and 1 part of ammonium sulfate both the lithium and the sodium-potassium mixture can be weighed as sulfates. It is necessary to deduct 0.5 mg. from the weight of lithium sulfate and add the same quantity to the weight of the sodium sulfate-potassium sulfate mixture.

The solubilities of the chlorides and perchlorates of sodium, potassium and lithium are given in Tables 24 and 25.

TABLE 24.—SOLUBILITY OF ALKALI CHLORIDES IN ISOBUTYL ALCOHOL

Salt	g. of Salt per 100 g. of Solvent
NaCl	0.00047
KCl	0.0008
LiCl	10.57

TABLE 25.—SOLUBILITY OF ALKALI PERCHLORATES
IN ISOBUTYL ALCOHOL

Salt	g. of Salt in 100 g. of Saturated Solution
NaClO ₄	0.78
KClO ₄	0.005
LiClO ₄	36.73

Determination of strontium and barium. The solubility of strontium bromide in isobutyl alcohol is approximately 8 g. of the salt per 100 g. of the solvent. Only approximately 0.011 g. of barium bromide dissolves in the same weight of solvent. This difference in solubility makes possible the separation of strontium and barium.^{6,7}

Procedure. Evaporate a solution containing about 0.5 g. of the alkaline earth nitrates several times with 50 ml. portions of sulfate-free hydrobromic acid to convert the nitrates to the bromides. Dry the residue at 100° C., add 2-3 ml. of isobutyl alcohol, and grind to a fine powder with a pestle while gradually adding an additional 10 ml. of the alcohol. Heat to 110° C. for 10 minutes with stirring. Allow the barium bromide to settle and decant the mixture through a filter that has been moistened with isobutyl alcohol. Rinse the dish and the pestle with a little of the alcohol but retain the crystals in the dish. Evaporate the filtrate in a weighed 25 ml. crucible heated to 100-110° C., and treat the residue, while still warm, with a few drops of water and 5 times as much finely powdered ammonium sulfate. Dry at 100° C., ignite carefully and weigh as strontium sulfate. A correction of 5 mg. of barium sulfate is applied for each extraction of the barium-strontium mixture. The factor for strontium oxide in strontium sulfate is 0.5642.

Barium and strontium may also be separated by treating the nitrates with concentrated hydrobromic acid as described above and drying the bromides at 180° C. The residue is then treated with absolute methyl alcohol and anhydrous isobutyl alcohol. The strontium bromide is removed by this treatment while the barium bromide remains as a crystalline, easily filterable salt.⁸

Determination of calcium. Calcium may be separated from strontium⁹ and barium¹⁰ by a procedure based on the fact that anhydrous calcium nitrate is soluble in isobutyl alcohol while strontium and barium nitrates are insoluble.

Isobutyl alcohol is also used with acetoacetic ester for the determination of calcium oxide and calcium hydroxide in the presence of anhydrous and hygroscopic calcium silicates¹¹ (page 392).

Determination of phosphates. Berenblum and Chain^{12,13} have used isobutyl alcohol in a colorimetric method for the determination of phosphates in biological fluids. The method consists of the removal of reducible phosphomolybdic acid from an aqueous solution by extraction with isobutyl alcohol, and the subsequent reduction of the compound to molybdenum blue with stannous chloride. In this way 1-100 γ of phosphorus can be determined. Since the extraction occurs readily over a wide range of acidity (0.05-1.5 N sulfuric acid) and is not affected by the presence of an excess molybdic acid, a considerable variation in the concentration of the reagents used does not bring about any interference in the formation of the color. To determine inorganic phosphorus proceed as follows:

Stannous chloride solution. Dissolve 10 g. of stannous chloride in 25 ml. of concentrated hydrochloric acid and dilute this solution to 200 times its volume with 1 N sulfuric acid.

Procedure. If the solution to be tested is strongly acid, neutralize and transfer 5 ml. of the neutral solution to a separatory funnel. Add 0.5 ml. of 10 N sulfuric acid, 2 ml. of distilled water, 2.5 ml. of 5 per cent ammonium molybdate solution and 10 ml. of isobutyl alcohol. Shake 1-2 minutes and discard the aqueous layer. Wash the isobutyl alcohol solution by shaking with two 5 ml. portions of N sulfuric acid, and then shake with about 15 ml. of the stannous chloride solution. Shake the mixture for 30 seconds and discard the aqueous layer. Pour the blue solution into a 10 ml. volumetric flask, wash the separatory funnel with ethyl alcohol, and dilute the solution to the mark with these washings and additional ethyl alcohol if necessary. Determine the resulting color in a colorimeter.

Fluoride, citrate, oxalate, nitrite and hypochlorite interfere with this procedure.

Determination of silver and chloride. Isobutyl alcohol and ether have been recommended in the Volhard titration of silver and chlorides, but according to Kolthoff¹⁴ this reagent is less satisfactory than others that have been proposed (page 60).

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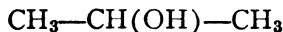
ISOPROPYL ALCOHOL

Synonym: Propanol-2

C_3H_8O

Mol. Wt. 60.09

Beil. Ref. I, 360.



Use: Detection of boron and chromium.

Determination of barium, calcium, copper, magnesium, nickel, potassium, sodium and strontium.

Isopropyl alcohol is a colorless liquid with slight odor resembling that of acetone. It boils at 82.5° C. and has a sp. gr. of 0.783. It is miscible with water, alcohol and ether.

Preparation of absolute isopropyl alcohol. Absolute isopropyl alcohol may be prepared from the commercial 91 per cent grade by a procedure described

by Gilson.¹ Shake the commercial product with 10 per cent of flake sodium hydroxide, separate from the aqueous layer which forms, shake with a second portion of sodium hydroxide, decant, and then distill. Collect the fraction boiling at 82-83° C.

Isopropyl alcohol may be substituted for ethyl alcohol in a great many types of analytical work.^{2,3} Isopropyl alcohol is particularly suitable as a substitute for ethyl alcohol because of the similarity of physical and chemical properties of these two compounds, and because of the absence of restrictions governing the purchase and use of the former. Isopropyl alcohol has proved extremely useful as a solvent in many analytical procedures. The alkali chlorides and sulfates are somewhat less soluble in isopropyl alcohol than in ethyl alcohol, and the rare earth chlorides are only very slightly soluble. The solubility of sodium chloride, potassium chloride and sodium sulfate in isopropyl alcohol ⁴ is given in Table 26.

TABLE 26.—SOLUBILITY OF ALKALI SALTS IN ISOPROPYL ALCOHOL

Solubility at 20° C. in Moles of Salt per Mole of Alcohol

Salt	Solubility
Sodium chloride	0.00096
Potassium chloride	0.001235
Sodium sulfate	0.000886

In addition to its use as a solvent for metallic salts, isopropyl alcohol has also been used as a solvent for dimethylglyoxime, which is used in the nickel determination, and for 8-hydroxyquinoline, which is used for the determination of copper. The accuracy of results obtained using these reagents is as great with isopropyl alcohol as with ethyl alcohol as the solvent. Since isopropyl alcohol is salted out by many inorganic compounds it enjoys only limited application as a solvent for inorganic reagents.²

Isopropyl alcohol may also be used as a reducing agent in certain analytical procedures. For example, the test for chromates by means of the Curtman reaction, which depends upon the reduction of alcohol with hexavalent chromium, may also be carried out satisfactorily by substituting isopropyl alcohol for ethyl alcohol. Isopropyl alcohol may also be substituted for ethyl alcohol in the turmeric test for borates, but the reaction is somewhat less sensitive than that with ethyl alcohol.

Many separations of metallic salts which depend upon their different solubilities in isopropyl alcohol are possible.² For example, calcium may be separated from barium, or calcium from magnesium, and potassium and sodium chlorides from magnesium chlorides with the aid of isopropyl alcohol.

Isopropyl alcohol may be used in the determination of calcium and strontium when the latter are precipitated as their sulfates, since these compounds are less soluble in aqueous isopropyl alcohol solution than in water. Isopropyl

alcohol may also be used to wash precipitates free from contaminating substances.²

The ionization constant of acetic acid in 90 per cent isopropyl alcohol is $10^{-6.45}$ as compared to $10^{-4.75}$ in water; hence, solutions of bases in 90 per cent isopropyl alcohol can be titrated with 0.5-1.0 N hydrochloric acid with greater precision than in water.⁵

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MANNA

Use: Determination of boron.

Manna is obtained by allowing the sap of certain trees to evaporate. It consists of 40-60 per cent mannitol; 12-16 per cent mannotetrose; 6-16 per cent mannose; glucose; mucilage and fraxin. It is obtained largely from Sicily and southern Italy. One gram dissolves in about 5 ml. of water and 150 ml. of 90 per cent alcohol.

Determination of boric acid. According to Iles,¹ manna can be used satisfactorily in place of glycerol for the titrimetric determination of boric acid. A solution of manna does not keep well, because upon standing for a few days a precipitate forms. A fresh solution of the necessary strength is prepared for each estimation. It is neutralized and added in the same way as glycerol (page 102). According to Iles,¹ about 5 g. in a solution is equivalent to 25 ml. of 80 per cent glycerol, but Mellon and Morris² state that 7 g. should be used for the determination. The reagent should be examined before use since the mannitol content varies considerably in different samples. The waxy portion should not be used.

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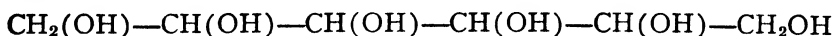
MANNITOL

Synonym: d-mannite, d-mannitol, hexanehexol



Mol. Wt. 182.17

Beil. Ref. I, 534.



Use: Detection of boron.

Determination of boron, germanium and vanadium.

Mannitol is a polyhydric alcohol obtained from ivory nut shavings and manna. It is a white crystalline solid melting at 166-166.5° C. One gram of the alcohol

dissolves in about 5.5 ml. of water and 83 ml. of alcohol. It is more soluble in hot water but is insoluble in ether.

Detection and determination of boric acid. When a dilute solution containing boric acid is neutralized to pH 7.0, and treated with mannitol, the solution becomes acid. Similarly, if a solution of mannitol is made barely alkaline and then treated with boric acid, the solution becomes acid. This behavior of mannitol has been used for the detection of boric acid and borates.^{1,2}

Procedure. Heat a 1:1 mixture of recrystallized mannitol and water to boiling and add bromthymol blue which has been adjusted to the transition color. Then add 0.01 N sodium hydroxide until the mixture is faintly alkaline. Add the same indicator to the solution to be tested for boric acid and bring to the same shade as that of the mannitol solution with 0.01 N sodium hydroxide or hydrochloric acid. When the two solutions are mixed, a complete decolorization occurs with as little as 2×10^{-8} g. of boron per ml. of solution. By mixing 1 drop of the solution to be tested with a drop of the reagent on a spot plate 10^{-9} g. of boron can actually be detected.

When a solution of boric acid is mixed with mannitol, the boric acid reacts as a strong acid and may be titrated with a standard base.³⁻¹¹ Glycerol and other polyhydric alcohols have been used for a similar determination, but Gilmour⁸ states that mannitol is eleven times as effective as glycerol. The following procedure may be taken as typical of the boric acid titrations using mannitol.³

Procedure. Separate the boric acid by volatilizing as the methyl ester, and collect the distillate in a sodium hydroxide solution. Distill the methyl alcohol and add 3 drops of 0.1 per cent methyl orange for each 10 ml. of the borate solution. Carefully neutralize with hydrochloric acid until the color changes from yellow to orange. Boil to expel carbon dioxide and then add alkali until the solution is barely orange in color. For each 10 ml. of solution add 1 g. of mannitol, 4 drops of 0.4 per cent α -naphtholphthalein and finally titrate with 0.1 N barium hydroxide solution until a green color is obtained. One ml. of 0.1 N alkali is equivalent to 0.0035 g. of B_2O_3 .

Prideaux⁴ recommends the use of sufficient sodium chloride to saturate the borate solution, and states that the titration is improved in this manner.

Jones¹² has based a method for titrating boric acid upon the fact that a solution of boric acid becomes much more strongly acid when mixed with mannitol; and further, that boric acid in solution in moderate quantity has no action upon a solution containing potassium iodide and iodate. Therefore if a solution of a borate is treated with a mineral acid, the excess mineral acid may be destroyed by the addition of potassium iodide and iodate while the free boric acid is unaffected. After destroying the iodine set free in the reaction with sodium thiosulfate, the free boric acid can be titrated with a standard base in the presence of mannitol.

Recently Ruehle and Shock¹⁸ have published a method for the potentiometric titration of small quantities of boron in which mannitol is used. Results obtained with quantities of boron ranging from 10 to 50 mg. are satisfactory.

Determination of germanium. Germanic acid, like boric acid, is capable of forming a complex with mannitol which acts as a strong acid and can be titrated with standard base.¹⁴ Tchakirian^{15,16} has used a procedure based on this principle for the determination of germanium. Ten grams of GeO_2 dissolves in 1 liter of water containing 20 g. of mannitol. In the presence of mannitol this solution can be titrated with sodium hydroxide toward which it reacts as a monobasic acid. Phenolphthalein is used as the indicator. If 20 g. of calcium chloride or strontium chloride is added to 10 ml. of germanium oxide solution, it reacts as a dibasic acid. Germanium may also be titrated iodometrically. If an aqueous solution of germanic acid is treated with a mixture of potassium iodide and potassium iodate and allowed to stand for 3 hours, one atom of iodine is formed for each atom of germanium. In the presence of strong electrolytes, and after standing 12 hours, 1 mole of iodine is formed for each atom of germanium. This makes possible the titration of germanium in the presence of strong acids. The strong acid is first eliminated by treating with potassium iodide and potassium iodate in the presence of starch, and the solution is then carefully decolorized with sodium thiosulfate. Then after adding mannitol and allowing to stand for 3 hours, the germanium is titrated indirectly with thiosulfate. When GeO_2 is dissolved in water, the saturated solution contains about 0.8 per cent of germanium, probably as H_2GeO_3 . After the addition of mannitol, an acid is probably formed which corresponds to $\text{H}_2\text{Ge}_2\text{O}_5\text{M}_n$, in which "M" represents 1 mole of mannitol and "n" is 2 or more. The compound $\text{H}_2\text{CaGeCl}_3\text{O}_3$ may be formed in the presence of a strong electrolyte such as calcium chloride.

Determination of vanadium. Salts of tetravalent vanadium liberate equivalent quantities of free acid when treated with mannitol and other polyhydroxy compounds.^{17,18,19} If the free acid in the tetravalent vanadium salt solution is previously determined, the vanadium can be indirectly estimated by titrating the free acid formed on adding mannitol to the mixture.

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METHYL ALCOHOL CH_4O

Mol. Wt. 32.04

Beil. Ref. I, 273.

 CH_3OH **Use:** Detection of boron and potassium.

Determination of aluminum, barium, boron, calcium, magnesium, potassium, sodium and strontium.

Methyl alcohol is a colorless, neutral liquid possessing a faint odor resembling that of ethyl alcohol. It boils at 64.6°C . and has a sp. gr. of 0.7928. It is miscible with water in all proportions, and also with most organic solvents.

Separation of calcium and magnesium. Various investigators^{1,2,3} have shown that methods based on the difference in solubility of calcium sulfate and magnesium sulfate in ethyl alcohol solutions are not very satisfactory for the separation of calcium and magnesium. The principle sources of error are the noticeable solubility of calcium sulfate in solvents of low ethyl alcohol content, and the slight solubility of magnesium sulfate in solutions having an ethyl alcohol concentration great enough to precipitate calcium sulfate quantitatively. Stolberg¹ proposed a solvent consisting of 10 parts of ethyl alcohol and 90 parts of methyl alcohol to replace the ethyl alcohol solutions previously used. This method proves to be satisfactory but is time consuming. Willard and Smith⁴ first suggested the use of methyl alcohol alone for the separation of calcium and magnesium as the sulfates, and recommended that the precipitation be made from a perchlorate solution. Caley and Elving⁵ suggest 90 per cent methyl alcohol as a medium for the precipitation of calcium sulfate. The addition of 1 ml. of concentrated sulfuric acid and 90 ml. of methyl alcohol to 9 ml. of solution to be analyzed will cause the complete precipitation of calcium as the sulfate. The following procedure gives satisfactory results:

Procedure. Add 1-2 ml. of 9 N sulfuric acid to the solution to be analyzed and evaporate to 5 ml. Then add 15 ml. of water and precipitate calcium by the slow addition of 180 ml. of methyl alcohol with constant stirring. Allow the mixture to stand until precipitation is complete and filter through a weighed filter crucible. Wash with 90 per cent methyl alcohol, first by decantation, and then by stirring the precipitate collected in the filtering crucible with a stream of wash liquid. Allow the precipitate to remain in contact with each portion of the wash liquid for a few minutes. Dry the crucible and contents for 30-45 minutes at 110°C . and then ignite for 30-45 minutes at $400\text{--}450^\circ\text{C}$. Cool in a desiccator and weigh as anhydrous calcium sulfate. The factor for calcium oxide is 0.4119.

Separation of barium and strontium. A mixture of methyl alcohol and isobutyl alcohol may be used for the separation of barium and strontium bromides. Details of this procedure are described on page 109 in the section on isobutyl alcohol.^{6,7}

Detection and determination of the alkali metals. Methyl alcohol is used in various separations required for the analysis of the alkali metals, and is also used to alter the properties of the reaction media to decrease the solubility of alkali salts formed in the analysis of this group. For example, methyl alcohol has been used in the precipitation of potassium as the bitartrate⁸ and for the separation of sodium and potassium.⁹⁻¹² Celsi¹³ has used methyl alcohol in the following test for potassium:

Procedure. To 10 ml. of pure methyl alcohol, add 1 drop of a solution containing 7 g. of cobalt nitrate dissolved in 50 ml. of 80 per cent methyl alcohol, and 1 drop of a solution containing 19 g. of sodium thiosulfate in 50 ml. of water. When a violet color has developed in this reagent, add 1-4 drops of the solution to be tested. A sky-blue precipitate forms with potassium. This reaction is said to be very sensitive.

Separation of beryllium. Beryllium may be separated from magnesium and the alkaline earths by precipitating as beryllium hydroxide. This compound is formed by hydrolysis. Ammonium nitrite is added to the reaction mixture to keep the hydrogen-ion concentration low, and methyl alcohol is used to remove the liberated nitrous acid as the methyl ester. The method is not satisfactory with barium, since ammonium nitrite may contain some sulfate.¹⁴

Determination of aluminum. A mixture of methyl alcohol and bromine may be used for the separation of aluminum and aluminum oxide. This provides a convenient method for the determination of aluminum oxide in aluminum metal. This use is illustrated by a procedure described by Steinhauser.¹⁵

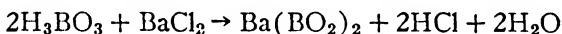
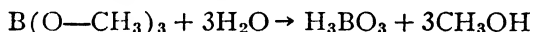
Procedure. Treat 5 g. of metal filings with 250 ml. of methyl alcohol and 20 ml. of bromine. Cool, if the reaction becomes violent, but finally heat to dissolve all the aluminum. Filter, wash the residue with methyl alcohol and ignite in a platinum crucible. Remove silica from the residue with hydrogen fluoride and sulfuric acid and weigh the impure aluminum oxide. Fuse with potassium pyrosulfate, extract with dilute sulfuric acid and determine the aluminum colorimetrically with eriochromecyanine.

Detection and determination of boron. Methyl alcohol has been extensively used in the detection and the determination of boric acid. Many schemes have been proposed in which the boric acid is separated from accompanying substances by converting to the volatile methyl ester and distilling.¹⁶⁻²² The methyl borate separation may be used as a preliminary to the well known turmeric test,¹⁸ or it may be used as a part of the flame test for boron. The usual procedure consists in treating a borate with sulfuric acid and ethyl alcohol and igniting the mixture which contains the ethyl ester. A green flame appears if boron is present. Unless an excess of acid is present, however, the test remains negative. According to Pieszczyk,²² the acid is unnecessary if ethyl alcohol is replaced with methyl alcohol. Methyl borate, like ethyl borate, burns with a green flame. The green color is easily distinguished in the presence of an excess of sodium as sodium tetraborate.

Methyl alcohol is also used for the separation of boric acid as a preliminary to the determination of boron.²³⁻³³ For details of this separation, see section on turmeric. The final determination may be carried out by various procedures. A colorimetric method with turmeric^{34,35} is described in the section on turmeric.

Stahl^{36,37} has suggested a method whereby 0.3 mg. or more of B_2O_3 can be determined with an accuracy of 0-15 per cent. This procedure is based upon forming methyl borate and comparing the color of the flame obtained when the alcohol containing the ester is burned with that of standards containing known quantities of boron. The standards are prepared by adding known quantities of boron to 100 volumes of methyl alcohol and 20 volumes of sulfuric acid. The standards and unknown are burned in three burners under standardized conditions.

Manning and Lang³⁰ have used methyl alcohol for the separation of boric acid as a preliminary to the subsequent gravimetric determination of boric acid as the barium salt. This determination is based on the following equations:



The boron may also be determined indirectly by titrating the hydrochloric acid liberated in the above reaction. Boric acid may also be titrated with a standard base after adding glycerol or mannitol. Calfee and McHargue³⁸ have ignited natural gas which is saturated with methyl borate in methyl alcohol in a stream of oxygen for the spectroscopic determination of boron.

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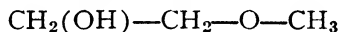
METHYL CELLOSOLVE

Synonym: Ethylene glycol monomethyl ether, 2-methoxyethanol

$C_3H_8O_2$

Mol. Wt. 76.09

Beil. Ref. I, 467.



Use: Determination of iron, sulfate and carbon disulfide.

Methyl cellosolve is a colorless liquid, having a sp. gr. of 0.975. It boils at 124° C. and is miscible with water.

Determination of iron. Many procedures for determining iron colorimetrically have been based upon the red color produced by the reaction between the thiocyanate ion and ferric iron. Winsor¹ has used a solution of 10 g. of ammonium thiocyanate in sufficient methyl cellosolve to make the total volume 250 ml. as a reagent for the determination of iron. The color produced is nearly twice as strong as that obtained with an aqueous solution of ammonium thiocyanate. The reagent should be stored 24 hours in a dark place before being used for the determination. This reagent is subject to photochemical change and becomes yellow on standing in light, which somewhat impairs its usefulness. The evaporation loss, however, is less, and the color obtained is stronger than with water-acetone mixtures, which are frequently used for the same purpose.

Determination of carbon disulfide. Carbon disulfide reacts with diethylamine in the presence of cupric ions to form a yellow or golden brown coloration. Morehead² has used this reaction for the detection and determination of carbon disulfide in air. The color obtained by using a solution of diethylamine in methyl cellosolve is more intense and more stable than is obtained when an alcoholic solution is used (see section on diethylamine).

Determination of sulfate. A solution of tetrahydroxyquinone which is used as an indicator in the determination of sulfates may be prepared by dissolving 0.15 g. of the indicator in 1 ml. of water and diluting with 2 ml. of methyl cellosolve. This solution is stable for about 18 hours.³

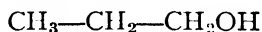
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PROPYL ALCOHOL



Mol. Wt. 60.09

Beil. Ref. I, 350.



Use: Determination of calcium and magnesium.

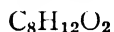
Propyl alcohol is a colorless liquid having a sp. gr. of 0.804. It boils at 96-98° C. It is miscible with water, alcohol and ether.

Determination of calcium and magnesium. Winkler^{1,2} has suggested the use of propyl alcohol in preparing a standard solution of potassium palmitate for the determination of calcium and magnesium. This is done to prevent the separation of palmitic acid. When ethyl alcohol is used, palmitic acid separates at temperatures below 15° C.

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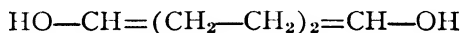
QUINITOL

Synonym: Hexahydroquinol, cyclohexandiol-1,4



Mol. Wt. 116.16

Beil. Ref. VI, 741.



Use: Detection of nitrate.

Quinitol occurs in two forms. The *cis* form occurs as prisms, melting at 100-102° C. It dissolves readily in water, alcohol and acetone, but is only slightly soluble in ether and chloroform. The *trans* form melts at 139° C. It dissolves readily in water and alcohol.

Preparation: Add 260 g. of 3 per cent sodium amalgam to a cooled solution of 10 g. of cyclohexandione-1,4 and 4 g. of sodium bicarbonate dissolved in 100 ml. of water. Pass carbon dioxide through the mixture while adding the amalgam.¹

Detection of nitrate. A solution of quinitol dissolved in 2:3 sulfuric acid gives a precipitate of nitroquinitol when added to solutions containing nitrate.²

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CHAPTER IX

PHENOLS

PHENOLS, in which a hydroxyl group is attached to an aromatic nucleus, are more strongly acidic than alcohols. Many of these compounds possess valuable analytical properties. It is characteristic of phenolic compounds generally that they form colored compounds with ferric iron and with pentavalent arsenic and antimony.^{1,2} Many analytical reactions are based on this behavior. Colored polyhydroxy aromatic compounds form color-lakes with such metals as aluminum, beryllium, magnesium and the alkaline earths.³ Ring structures may be formed when the acidic hydroxyl group is properly located with respect to a nitrogen atom, or other coordinating atom, and the resulting chelate salts are frequently valuable for the detection and determination of such metals as cobalt, nickel and copper. Many phenolic compounds such as the nitrosonaphthols 8-hydroxyquinoline and salicylaldehyde are included in other sections. Phenols are also used as coupling agents in reactions for nitrites, which are based on the Griess reaction. Some polyphenols, such as hydroquinone, are widely used as reducing agents in inorganic analysis. Still other phenols are analytically useful because of the ease with which the aromatic nucleus may be substituted, as with nitric acid. Titanic, columbic, tantallic and stannic acids react with phenols to yield color reactions.

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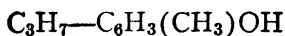
CARVACROL

Synonym: 2-Hydroxy-p-cymene, isopropyl-o-cresol, 1-methyl-4-isopropyl-2-hydroxy-benzene

$C_{10}H_{14}O$

Mol. Wt. 150.21

Beil. Ref. VI, 527.



Use: Detection of antimony and arsenic.

Carvacrol is a colorless liquid which is found in thyme and summer savory. It has an odor similar to that of thymol. It boils at 237-238° C. and has a sp. gr. of 0.976. It is insoluble in water but is freely soluble in alcohol and ether.

Detection of antimony and arsenic. A mixture of 1 drop of carvacrol and 1 ml. of chloroform gives a brownish-red to garnet-red color with a chloroform solution of antimony pentachloride. This solution becomes violet-red on dilution with chloroform.¹ Arsenate may be detected by the following procedure:

Procedure. A mixture of 1 drop of carvacrol and 0.02 g. of sodium arsenate and 1 ml. of sulfuric acid yields an olive-green color. On heating, a garnet-red color appears. This test may also be carried out as follows: Mix 1 drop of carvacrol, 0.5 ml. of alcohol, 2 ml. of sulfuric acid and 0.02 g. of sodium arsenate. A pale red color appears, and on heating this develops into a deep red.¹

1. L. Ekkert, *Pharm. Zentralhalle*. **75**, 49, 50 (1934).

CREOSOTE

Use: Detection of antimony.

Creosote is a coal tar fraction containing a mixture of phenols, but chiefly cresol and guaiacol. It is an almost colorless or yellowish oily liquid with a characteristic smoky odor and a caustic burning taste. Its sp. gr. is not below 1.076. It begins to boil at about 203° C., and about 90 per cent by volume distills between 203-220° C. It is miscible with alcohol, chloroform and ether.

Detection of antimony. A solution prepared by adding a drop of creosote to 1 ml. of chloroform is colored deep brown and then garnet-red with a chloroform solution of antimony pentachloride.

1. L. Ekkert, *Pharm. Zentralhalle*. **75**, 49, 50 (1934).

o-CRESOL Synonym: o-Hydroxytoluene, 1-methyl-2-hydroxybenzene
 C_7H_8O Mol. Wt. 108.13 Beil. Ref. VI, 349.
 $CH_3-C_6H_4-OH$

Use: Detection of nitrate, arsenate, and antimony pentachloride.

This compound consists of colorless crystals or occurs as a liquid which darkens with age and on exposure to air and light. It has a phenolic odor. It melts at 30° C. and boils at 191-192° C. It is soluble in about 40 parts of water, and is miscible with alcohol chloroform and ether.

Preparation: Dissolve 15 parts of o-toluidine in 500 parts of water and 15 parts sulfuric acid (d. 1.8), and add about 12 parts of potassium nitrite in water. Heat gradually by the introduction of steam, and distill the o-cresol with steam. Dissolve the distillate in sodium hydroxide, filter, acidify the filtrate with sulfuric acid, and extract the o-cresol with ether. Evaporate the ether, and purify by distillation in a stream of carbon dioxide.¹

Detection of nitrate. Nitrates may be detected with o-cresol even in the presence of nitrites.²

Procedure. Prepare a cold solution of 50 mg. of o-cresol by triturating in a glass mortar with 10 ml. of concentrated hydrochloric acid, and add 0.01-1.0 g. of the substance to be tested, and 0.2 g. of sodium nitrite. In about 1 minute, if nitrate is present, a dichroic solution is obtained which is deep green

in reflected light, and crimson or purple-red in transmitted light. In this way less than 0.001 g. of nitrate can be detected.

This reaction is claimed to be specific and sensitive. Bromides and iodides do not interfere with this reaction, although bromides and ethyl alcohol make the test less sensitive.

Russwurm^{3,4} uses cresol and concentrated sulfuric acid for the test, and finally makes the mixture alkaline with ammonium hydroxide.

Detection of arsenate. Arsenate ions may be detected by means of a reaction with o-cresol.⁴

Procedure. When approximately 0.01 g. of sodium arsenate is scattered in a mixture of 0.01 g. of o-cresol and 3 drops of sulfuric acid, a bright rose or flesh color gradually appears. This color changes to gray, and on heating becomes dark red and afterward brown.

Reagent for antimony pentachloride. Ekkert⁴ has used o-cresol as a reagent for antimony pentachloride. Approximately 0.03 g. of o-cresol in 1 ml. of chloroform gives a rust-brown color with a chloroform solution of antimony pentachloride.

1. F. Tiemann and C. Schotten, *Ber.* 11, 769 (1878).
2. A. H. Ware, *Analyst.* 52, 332-4 (1927); *C.A.* 21, 2629 (1927).
3. K. Russwurm, *Pharm. Zentralhalle.* 40, 516 (1899); *Chem. Zentr.* II, 593 (1899).
4. L. Ekkert, *Pharm. Zentralhalle.* 75, 49-51 (1934).
5. Russwurm, *J. Soc. Chem. Ind.* 18, 1052 (1899).

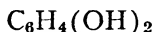
HYDROQUINONE

Synonym: Hydroquinol, quinol, p-dihydroxybenzene



Mol. Wt. 110.11

Beil. Ref., VI, 836.



Use: Detection of arsenic, copper, gold, nitrate, nitrite, phosphorus, rhenium, alkalinity of solid salts, silver, titanium and tungsten.

Determination of arsenic calcium, fluorine, gold, iron, magnesium, nitrate, phosphorus, selenium, silicon, silver, and tungsten.

Hydroquinone consists of colorless or white crystals. It melts at 168-169° C. and boils at 285-287° C. It is moderately soluble in water but is freely soluble in alcohol and ether. It is only slightly soluble in benzene. Solutions of this reagent become brown in air due to oxidation, and the oxidation proceeds very rapidly in the presence of an alkali. Store the compound in a tightly closed bottle and protect from light.

Preparation. *Benzoquinone:* Add 23 g. of aniline to a mixture of 100 ml. of pure concentrated sulfuric acid and 500 ml. of water and cool to 10° C. or lower. To this solution gradually add, with stirring and cooling in an ice bath, a

solution of 30 g. of sodium dichromate in 75 ml. of water. The temperature should not rise above 10° C. during this addition. Allow the mixture to stand in a cool place overnight, and then add slowly and with stirring an additional 40 g. of sodium dichromate in 120 ml. of water. Allow the mixture to stand for 6 hours and filter through a large Buchner funnel. Wash the solid with a little water, and then extract the filtrate twice with 500 ml. portions of ether. Distill the ether with steam, and divide the distilled ether into two portions, which are used to extract the filtrate again. Again steam distill to remove the ether. Collect the crude benzoquinone from the funnel, and add to that extracted with ether. Steam distill the benzoquinone and collect the compound in the receiver as beautiful golden-yellow crystals. Dry for a short time between filter paper and then dry in a desiccator over calcium chloride. Recrystallize from alcohol.

Hydroquinone: Suspend about 2 g. of benzoquinone in 50 ml. of water and while shaking, frequently saturate the suspension with sulfur dioxide. Allow to stand for some time and then extract the colorless liquid twice with ether. Dry the ether extract over calcium chloride and evaporate the ether. The residue of hydroquinone crystallizes. Purify by recrystallizing from a little water.

Detection and Determination of Phosphorus. Under suitable conditions molybdates react with phosphates, arsenates, silicates and certain other salts or acids to form heteropoly compounds, such as ammonium phosphomolybdate $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$ or silicomolybdic acid, $\text{H}_4[\text{Si}(\text{Mo}_3\text{O}_{10})_4]$. These complexes react with many reducing agents to yield molybdenum blue, which has been used for the detection and the determination of the various reducing agents or of the elements which function as the central atoms in the complex anion, such as phosphorus, arsenic and silicon.

Bell and Doisy¹ have employed the blue color produced by the reduction of phosphomolybdic acid with hydroquinone for the determination of phosphorus in urine and blood. The blue color is formed in an alkaline solution, but under these conditions fades fairly rapidly. In an acid solution in the first phase of the determination a stable green color is formed which is proportional to the phosphorus content, but this color was not used by Bell and Doisy¹ since urine and trichloroacetic acid blood filtrates frequently yield a turbidity when treated with an acid molybdate solution. Briggs,^{2,3,4} by a suitable modification of the foregoing procedure, obtained a practically pure green color with acid molybdate and hydroquinone. The green color of the acid solution, however, is less intense than the blue color formed in an alkaline solution and consequently is not so accurate when the phosphorus concentration is very low. This disadvantage, however, is offset by the stability of the green color.

Briggs^{2,3,4} also observed that when a little sodium sulfite is added to an acid solution containing a phosphate and molybdate and the mixture is then treated with hydroquinone, a blue color is formed and the intensity is greater than that of the green color described in the original procedure. The formation of this color does not depend upon the reduction of the phosphomolybdate by sulfur dioxide, since sodium sulfite, hydroquinone and an acid molybdate solution give no color when mixed.

Benedict and Theis⁵ have further modified the procedure by developing the color through heating of the solution, and Stoloff⁶ suggests the use of sodium succinate as a buffer to replace sodium sulfite.

The Bell-Doisy method. The conditions necessary for determining phosphorus by the Bell-Doisy method are described by Woods and Mellon⁷:

Reagents. *Hydroquinone solution:* A 2 per cent solution of hydroquinone in 0.03 N sulfuric acid.

Ammonium molybdate solution: A 5 per cent solution of ammonium molybdate in 1 N sulfuric acid.

Sodium sulfite solution: Dissolve 200 g. of sodium carbonate and 37.5 g. of sodium sulfite in sufficient water to make 1 liter of solution.

Procedure. Transfer the sample containing about 0.25 mg. of phosphorus to a 100 ml. flask, and to this add 5 ml. of the ammonium molybdate solution and 5 ml. of the hydroquinone solution. Allow to stand for 5 minutes and then add 25 ml. of the sodium sulfite solution. Dilute to the mark and measure the color immediately with a photoelectric spectrophotometer.

Since the solution becomes bluer with increasing basicity, and as the intensity of the color also increases under these conditions, the amount of sulfite solution added must be carefully controlled. Small changes in concentration of molybdenum and hydroquinone do not materially affect the color. There is little change in color on allowing the solution to stand from 1 to 25 minutes after adding the hydroquinone solution providing the measurement is made soon after the addition of the sodium sulfite solution. The color begins to fade immediately upon adding the sulfite, but no serious error is introduced if the reading is made within 10-15 minutes. The color conforms to Beer's law within the concentration range 0.1-10 p.p.m.

Many investigators⁸⁻²¹ have used the method of Bell and Doisy¹ for the determination of inorganic phosphorus in serum, plasma, urine and other biological materials, and others²²⁻²⁸ have used a similar method for determining lipid phosphorus in blood and plasma.

Myers and Shevsky²⁵ have prepared a series of standards so that in each determination one may be selected which contains phosphorus in an amount not exceeding that of the unknown by more than 0.25 mg. of phosphorus in 100 ml. of solution.

Urbach¹⁹ recommends the use of a Zeiss step photometer for the color determination. The method is claimed to be more accurate and to require less time than the usual colorimetric procedure, and requires no standard solution.

Denis²⁹ has found that oxalates and citrates, which are used to prevent the clotting of blood, interfere with the formation of the alkaline blue color produced according to the Bell-Doisy method.

Briggs method. Briggs^{2,3,4} describes the following procedure for the determination of phosphorus in blood or plasma:

Reagents. *Hydroquinone reagent:* Dissolve 0.5 g. of hydroquinone in 100 ml. of water and add a drop of concentrated sulfuric acid.

Ammonium molybdate solution: Dissolve 25 g. of ammonium molybdate in 300 ml. of water. Dilute this solution with a mixture of 75 ml. of concentrated sulfuric acid and 125 ml. of water.

Standard phosphate solution: Dissolve 0.4388 g. of potassium dihydrogen phosphate in a little water and dilute to 1 liter. Dilute 25 ml. of this solution to 200 ml. and mix well. Preserve with a little chloroform. Two ml. of this solution contains 0.025 mg. of phosphorus.

Procedure. Transfer a measured volume of plasma to a small Erlenmeyer flask and dilute with 3 volumes of water and 1 volume of 20 per cent trichloroacetic acid. Stopper the flask and shake vigorously for a few seconds and then allow to stand for 10 minutes. Filter through a dry ashless filter which is supported in a funnel resting in a long pyrex test tube and covered by a watch glass to prevent loss by evaporation.

Transfer 5 ml. of the filtrate, which is equivalent to 1 ml. of plasma, to a 10 ml. volumetric flask. Place 2 ml. of the standard phosphate solution in a similar flask, and then to each add 2 ml. of the molybdate solution, 1 ml. of a 20 per cent sodium sulfite solution, and 1 ml. of the hydroquinone solution and finally dilute to the mark with distilled water. Allow to stand for about 30 minutes for the full development of the color and then compare in a colorimeter.

It is not necessary to add trichloroacetic acid to the standard solution, but it is necessary to maintain the acidity within certain limits for color production. Sufficient acid is provided by 2 ml. of the molybdate solution for the formation of ammonium phosphomolybdate and its subsequent reduction. If, however, the total acidity after the addition of all reagents is greater than 2 N, no color is obtained.

Denis²⁹ has found that oxalates and citrates interfere with the formation of the alkaline blue color according to the Bell-Doisy method, but when these salts are present in the quantity required to prevent clotting of blood, they do not interfere with the formation of the blue color by the modified procedure of Briggs.

Briggs⁴ describes the following method for the determination of phosphorus in urine.

Reagents. All reagents are the same as those described for the determination of phosphorus in blood and plasma (see above) except the standard phosphate solution. This is prepared as follows:

Dissolve 0.4388 g. of potassium dihydrogen phosphate in a little water and dilute to 1 liter. Mix thoroughly and preserve with a little chloroform. One ml. of this solution contains 0.1 mg. of phosphorus.

Procedure. Place 1 to 5 ml. of acidified urine, or a quantity equivalent to about 0.5 mg. of phosphorus in a 100 ml. volumetric flask. In a similar flask

place 5 ml. of the standard phosphate solution. To each add water until the total volume is about 80 ml., and then add to each 5 ml. of the molybdate solution, 1 ml. of 20 per cent sodium sulfite solution and 1 ml. of hydroquinone solution. Dilute to the mark with distilled water and allow to stand for 30 minutes for full development of the color and then compare in a colorimeter.

The color formed in this procedure depends somewhat on the quantity of reagents used but more especially upon the length of time allowed after adding the reagents. Since the reaction is incomplete even after five days, the color measurement must be made at some definite time after preparing the solution.⁷ The Briggs modification may be applied over a concentration range of 0.5-12 p.p.m. of phosphorus, and the color conforms to Beer's law over this range.⁷ The Briggs modification of the Bell Doisy method has been very widely used particularly in the determination of phosphorus in blood and biological materials.³⁰⁻⁴⁶ This method has also been used to determine phosphate in soil extracts,⁴⁷ water,⁴⁸ milk⁴⁹ and sugar.⁵⁰

Rimington⁵¹ has shown that the color is markedly depressed if the concentration of ammonium sulfate is increased, although the final depth of color after a long period is virtually unaffected. Ammonium oxalate, sodium sulfate, sodium fluoride and sodium citrate all interfere with the color produced if present in sufficient quantity. Maitland and Robison³⁸ have used the Briggs method for the determination of phosphorus in blood, but have substituted a 5 per cent ammonium molybdate solution for the Briggs molybdate solution. Byall and Ambler^{50,52} have used the Briggs method to determine phosphorus and silicon in sugar. They report that silicon interferes with the phosphorus determination when the usual procedure is applied, but phosphorus and silicon may be determined together by application of a special technique. Then, after the removal of silicon as silicon dioxide by dehydration with nitric acid, the total phosphate is determined colorimetrically in the filtrate and silicon is determined by difference. Scarritt⁴⁸ reports that the greatest error in the determination of phosphorus in water is due to the presence of silica. Silica, like phosphate, causes a color with the reagent and also intensifies the color due to phosphate, causing errors as great as 100 per cent. By acidifying the solution properly it is possible to repress the ionization of the weak silicic acid to the point where it develops no noticeable blue color, while the stronger phosphoric acid is sufficiently ionized under these conditions to react with the molybdate and to produce a blue color proportional in intensity to the phosphorus concentration. It is important to prepare the phosphate standards with the same quantity of acid used in the samples since the quantity of acid influences the depth of color produced.

Reagents. Hydroquinone solution. Dissolve 23 g. of hydroquinone and 5 ml. of concentrated sulfuric acid in 1 liter of solution.

Ammonium molybdate solution: Dissolve 92.3 g. of ammonium molybdate and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{21} \cdot 4\text{H}_2\text{O}$ and 38 ml. of concentrated sulfuric acid in 1 liter of solution.

Standard phosphate solution: Dissolve 0.320 g. of trisodium phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in a little distilled water and dilute to 1 liter. One ml. of this solution is equal to 2 p.p.m. of phosphate in 40 ml. of water.

Alkaline sulfite solution: Dissolve 183 g. of sodium hydroxide and 16 g. of sodium sulfite in 1 liter of water.

Sulfuric acid solution: Mix 600 ml. of water and 300 ml. of concentrated sulfuric acid.

Procedure. To 40 ml. of the water to be analyzed, add 5 ml. of sulfuric acid and mix thoroughly. Then add 1 ml. of the ammonium molybdate solution and 1 ml. of hydroquinone solution. Shake vigorously and allow to stand for 5 minutes. Add 15 ml. of the alkaline sulfite solution and compare the blue color with that of standards similarly and simultaneously prepared. The color comparison should be carried out immediately.

Benedict and Theis method. Benedict and Theis ⁵ have proposed a modification of the Briggs method in which the color is claimed to be about three times as intense as in the latter procedure and does not change on standing even after several days. In this procedure the color is developed by heating the solution.

The following method is used for the determination of inorganic phosphate in blood:⁵³

Reagents. Hydroquinone reagent: Dissolve 30 g. of sodium bisulfite in 100 ml. of water in a 200 ml. graduated flask and add 1 g. of hydroquinone. Dilute to the mark and mix well.

Molybdate reagent: Add 25 ml. of 20 per cent sodium hydroxide solution to 20 g. of ammonia-free molybdic acid. Warm gently until solution is complete and allow to cool. Finally dilute to 250 ml. and filter if necessary.

Standard phosphate solution: Dissolve 0.4388 g. of potassium dihydrogen phosphate in a little water and dilute to 1 liter. Dilute 5 ml. of this solution to 100 ml. with water and mix thoroughly. Preserve with a little chloroform. One ml. of the diluted solution contains 0.005 mg. of phosphorus.

Procedure. Place 4 volumes of 10 per cent trichloroacetic acid in an Erlenmeyer flask and with gentle rotation add 1 volume of plasma or serum from a pipet that is calibrated for delivery. Close the flask with a clean, dry rubber stopper and shake vigorously. Filter at once through an ashless paper.

Place 5 ml. of the filtrate in a test tube and add 3 ml. of distilled water and 1 ml. of the molybdate reagent which is diluted just before using with an equal volume of concentrated sulfuric acid. Then add 1 ml. of the hydroquinone-sulfite reagent and mix well. Stopper loosely and place in a boiling water bath for 10 minutes. The resulting color should be compared with a standard solution containing 0.025 mg. of phosphorus in 5 ml. of solution that has been similarly and simultaneously prepared.

Heating for longer than 10 minutes will produce a little increase in color intensity in both standard and blood filtrate, but the proportionality remains the same at the end of an hour as after 10 minutes. The range of concentration for the Benedict and Theis method is 0.1 to 5 p.p.m., and the system conforms to Beer's law up to 3 p.p.m. Dutcher and co-workers⁵⁴ have used a similar method for determining phosphates.

Woods and Mellon⁷ have carried out a spectrophotometric study of the molybdenum blue reaction using the three modifications described above and a summary of their results is shown in Table 27, which is taken directly from their work.*

TABLE 27.—MOLYBDENUM BLUE REACTION WITH HYDROQUINONE
AS A REDUCING AGENT*

	Bell & Doisy	Briggs	Benedict & Theis
P concn. at 50% transmission, ^a p.p.m. phosphorus	1.65	2.62	1.06
Working range, 1-cm. cell p.p.m. phosphorus..	0.1-10	0.1-15	0.1-5
Time and temperature to develop color	5 min., 20-25°	30 min., 20-25°	25 min., 100°
Stability	15 min.	Changes ^b	10 hours
Effect of excess reagent	Slight decrease
Effect of excess reductant	Slight increase	Increase
Conformity to Beer's law, p.p.m. phosphorus..	0-10	0-12	0-3

* Reproduced by permission of copyright owners, the American Chemical Society.

^a For 1-cm. cell at 700 mμ.

^b Measurement must be made after definite time.

Stoloff method. Stoloff⁶ has studied the Bell-Doisy method and has observed that the color first developed is green, and that this later becomes blue upon the addition of sodium sulfite. Since sodium sulfite alters the pH of the solution, Stoloff⁶ has studied the effect of pH upon the color produced in the molybdenum blue reaction. In order to cover the pH range in which the color change was observed, the acidity of the ammonium molybdate reagent was changed from 3 N to 1 N sulfuric acid and varying quantities of 20 per cent sodium succinate were used instead of sodium sulfite. These studies led to the development of a modified procedure in which sodium succinate is employed.

Reagents. *Hydroquinone solution:* Dissolve 0.5 g. of hydroquinone in 100 ml. of distilled water containing 1 drop of concentrated sulfuric acid.

Ammonium molybdate reagent: Dissolve 5 g. of ammonium molybdate in 100 ml. of 1 N sulfuric acid.

Sodium succinate reagent: Dissolve 20 g. of sodium succinate (calculated as the anhydrous salt) in 100 ml. of distilled water.

Procedure. The phosphorus should be in the form of the orthophosphate, and the sample should be a clear colorless solution that is neutral or slightly acid to litmus. Place an aliquot of the sample, up to 15 ml. in volume and containing not more than 0.3 mg. of phosphorus, in a 25-ml. volumetric flask. If the aliquot used is less than 10 ml., dilute to 10 ml. with distilled water and add the following in the order given, mixing well after each addition: 2 ml. of ammonium molybdate solution, 2 ml. of hydroquinone solution, 2.5 ml. of sodium succinate solution. Dilute to 25 ml. with distilled water and measure the color at 460 $m\mu$ within 4 hours.

The reaction seems to be instantaneous and complete, and delay as long as 15 minutes in the addition of any of the reagents appears to have no effect upon the final result other than to slow the reduction of the molybdate before the buffer is added. Buffers other than sodium succinate may be used. The effective range of this method is 0.0 to 0.35 mg. of phosphorus, and within this range the system follows Beer's law closely.

Determination of magnesium. Magnesium may be estimated indirectly by precipitating as magnesium ammonium phosphate and determining the phosphorus present in the precipitate by converting to the phosphomolybdate and reducing with hydroquinone.^{42,55-61} This method is generally used for determination of small quantities of magnesium in urine, blood and tissue.

The following procedure, which is based on the Bell-Doisy reaction, may be used for estimating magnesium after the separation of calcium as the oxalate.^{62,63}

Reagents. *Hydroquinone reagent:* Dissolve 20 g. of hydroquinone in 1 liter of water and add 1 ml. of concentrated sulfuric acid.

Ammonium molybdate reagent: Dissolve 50 g. of ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$, in a liter of N sulfuric acid. Five ml. of this solution should give no color when treated with 5 ml. of the reagent solution, and after 5 minutes with 25 ml. of the carbonate-sulfite solution.

Carbonate-sulfite solution: Dissolve 15 g. of sodium sulfite in 100 ml. of water and add to 400 ml. of a 20 per cent sodium carbonate solution. Filter.

Standard phosphate solution: Dissolve 4.388 g. of potassium dihydrogen phosphate in water and dilute to 1 liter. Mix thoroughly and preserve with a little chloroform. One ml. of this solution contains 1 mg. of phosphorus. The weight of magnesium in the sample is found by multiplying the weight of phosphorus by 0.7838.

Procedure. Precipitate calcium⁶⁴ by a method described in the section on calcium determination (page 131). With the aid of a pipet transfer 5 or 10 ml. of the clear supernatant liquid to a 25-ml. centrifuge tube and add dropwise 1 ml. of diammonium hydrogen phosphate and then 2 ml. of 10 per cent ammonium hydroxide solution, also added dropwise. Scratch the sides of the tube thoroughly and allow the mixture to stand overnight. Centrifuge the mixture

to remove the precipitate, wash twice with 10 per cent ammonium hydroxide and once with ammoniacal alcohol and then dry at 70° C.

Dissolve the precipitate in 10 ml. of 0.1 N hydrochloric acid and transfer the solution to a 25-ml. volumetric flask. In a second 25-ml. volumetric flask place 5 ml. (0.05 mg. of P) of the standard potassium dihydrogen phosphate solution, and to both flasks add 5 ml. of phosphate-free distilled water, 1 ml. of the molybdate solution and 2 ml. of the hydroquinone solution. Allow to stand for 5 minutes and to each flask add 10 ml. of the carbonate-sulfite solution. Dilute to 25 ml., mix thoroughly, allow to stand 5 or 10 minutes and compare in a colorimeter. To determine the quantity of magnesium present, multiply the weight of the phosphorus found by 0.7838.

The foregoing procedure gives results which are somewhat low. This may be due to the incomplete precipitation of magnesium or to solution of the precipitate during washing, but the loss does not exceed about 3 per cent if proper precautions are taken.^{58,59}

According to Hammett and Adams,⁵⁶ the separation of magnesium ammonium phosphate by centrifuging is preferable to filtration, because even the best acid-washed asbestos or pulp made from the best grade of filter paper contains sufficient phosphate or other substances capable of giving a blue color to cause an error in the colorimetric determination.

Magnesium may also be determined by a modification of the above procedure based upon the reduction of the phosphomolybdate by the method of Briggs.^{2,3,4} The following procedure may be used for the determination of magnesium in urine:⁶³

Procedure. If albumin is absent, transfer 2 ml. of the clear acid urine to a pyrex test tube and add 1 drop of methyl red solution. Then add 1:3 ammonium hydroxide dropwise until the color changes to yellow. If too much ammonium hydroxide is used, add 5 per cent acetic acid. Next add 1 ml. of 4 per cent ammonium oxalate solution and rub the sides of the tube with a policeman to precipitate calcium oxalate. Allow the mixture to stand for 2 hours, but do not filter. If albumin is present, this must be destroyed by wet or dry ashing and the residue dissolved and treated as described above for the precipitation of calcium.

To the sample contained in a pyrex test tube marked at 15 ml., add 1 ml. of a 2 per cent solution of monopotassium phosphate and 1 ml. of concentrated ammonium hydroxide. Scratch the tube to aid in precipitation of magnesium ammonium phosphate and allow to stand for 4 hours. Centrifuge for 10 minutes at 1500 r.p.m. and decant the clear upper layer. Wash the precipitate with 20 ml. of a mixture of 200 ml. of 95 per cent alcohol and 50 ml. of concentrated ammonium hydroxide. Break up the precipitate with a rod fitted with a policeman to aid in the washing. Again centrifuge, decant and wash.

Dissolve the magnesium ammonium phosphate in 10 ml. of 0.01 N hydrochloric acid, and add 1 ml. of a 5 per cent ammonium molybdate solution and 1 ml. of the reagent containing 30 g. of sodium bisulfite and 1 g. of hydroquinone in 200 ml. of phosphorus-free water. Dilute to 15 ml., allow to stand 30 minutes,

and compare with a standard similarly and simultaneously prepared. The standard is prepared by dissolving 0.4388 g. of potassium dihydrogen phosphate in water and diluting to 1 liter. One ml. of this solution contains 0.1 mg. of phosphorus. Each ml. of the standard corresponds to 0.0784 mg. of magnesium.

To determine magnesium in organic samples by the foregoing method, ash with nitric and perchloric acids and proceed as described above.

Determination of calcium. Like magnesium, calcium may be determined indirectly by converting to the phosphate, with the subsequent formation of phosphomolybdate and reduction to molybdenum blue.^{2,65,66} Best results are obtained by first separating the calcium as the oxalate and then converting to the phosphate. Arsenic must be absent, since it is determined by a similar method.

Procedure. Transfer 10 ml. of the solution to be analyzed, containing about 0.2 mg. of calcium, to a test tube marked at 15 ml. and add 1 drop of a methyl red solution. Then add 1:3 ammonium hydroxide solution with stirring until the color changes to yellow, and then add a few drops of 5 per cent acetic acid to the appearance of a faint pink color. Add 1 ml. of 4 per cent ammonium oxalate solution and scratch the sides of the tube with a policeman until a precipitate forms. Allow the mixture to stand for 2 hours and centrifuge for 10 minutes at 1500 r.p.m. Remove the supernatant liquid (this may be saved for the determination of magnesium by the above procedure), and wash the precipitate with 5 ml. of 0.5 per cent ammonium oxalate solution and again centrifuge. Remove the washings by decantation and add to the original supernatant liquid if magnesium is to be determined.

Treat the residue of calcium oxalate with 1 drop of concentrated hydrochloric acid and 0.5 ml. of 30 per cent hydrogen peroxide. Cover and heat for 30 minutes in a boiling water bath, and add 0.5 ml. of a 2 per cent solution of monopotassium phosphate and 3 drops of concentrated ammonium hydroxide. Allow to stand for 30 minutes and add 20 ml. of a solution containing 200 ml. of 95 per cent alcohol and 50 ml. of ammonium hydroxide per liter. Centrifuge the mixture for 10 minutes and remove the supernatant liquid by decantation. Again wash with a second 20-ml. portion of the above ammoniacal alcohol mixture, stir, rub the sides of the tube with a policeman and again centrifuge. Remove the liquid by decantation and to the residue of calcium phosphate add 5 ml. of water, 1 ml. of a 5 per cent ammonium molybdate solution and 1 ml. of a reagent containing 1 g. of hydroquinone and 30 g. of sodium bisulfite in 200 ml. of phosphorus-free water. Dilute to 15 ml. and allow to stand for 30 minutes. Compare with 5 ml. of a standard solution containing 0.1 mg. of phosphorus per ml. This is prepared by dissolving 0.4388 g. of potassium dihydrogen phosphate in water and diluting to 1 liter. Each ml. is equivalent to 1.291 mg. of calcium.

Determination of Silicon. Silicon may be determined colorimetrically by converting to silicomolybdic acid, which in turn is reduced to molybdenum

blue. Pincussen and Roman⁶⁷ have used the following method for determining silicon in organic materials.

Reagents. *Hydroquinone solution:* Dissolve 20 g. of hydroquinone in a little water and dilute to 1 liter. Add 1 ml. of concentrated sulfuric acid and store in a dark bottle.

Molybdate solution: Purify ammonium molybdate as follows: dissolve 150 g. of pure ammonium molybdate in 1 liter of water with the addition of 1 liter of 25 per cent nitric acid. Add 200 g. of pure ammonium nitrate. Allow to stand in a warm place for 1 day or until a white precipitate has formed on the bottom of the vessel. Filter, and to the filtrate add a double quantity of absolute alcohol, and then add ammonia until the mixture is alkaline. Filter. Pure ammonium molybdate remains. Dry in a desiccator over calcium chloride.

The molybdate reagent is prepared by dissolving 50 g. of purified ammonium molybdate in 1 liter of N sulfuric acid with gentle warming. Filter if necessary.

Carbonate-sulfite solution: Mix 1 liter of 20 per cent sodium carbonate solution with 500 ml. of a 15 per cent sodium sulfite solution.

Standard silicon solution: Dissolve 2.131 g. of pure silicic acid in 40 ml. of N sodium hydroxide and dilute to 1 liter. One ml. of this solution contains 1 mg. of silicon.

Magnesia mixture: Dissolve 55 g. of crystalline magnesium chloride and 105 g. of ammonium chloride in 1 liter of water and add a few drops of concentrated hydrochloric acid.

Carbonate mixture: Mix equal parts of anhydrous potassium and sodium carbonate.

Procedure. Fuse a quantity of the material containing about 1 mg. of silicon with 5 times as much of the carbonate mixture in a platinum crucible. Remelt with potassium nitrate if necessary to destroy any organic substances. Cool, leach with water, filter, and neutralize the filtrate with sulfuric acid. Transfer to a centrifuge tube and make alkaline with ammonium hydroxide and then add magnesia mixture. Allow to stand for 24 hours, centrifuge, and wash the precipitate with 10 per cent ammonium hydroxide solution.

Evaporate the filtrate and washings to a small volume with dilute sulfuric acid and transfer to a 25 ml. flask. Add 1 ml. of molybdate reagent and 2 ml. of hydroquinone solution. Allow to stand 5 minutes and add 5 ml. of carbonate-sulfite solution. Shake, dilute to the mark, allow to stand for 5 minutes and compare with standard silica solutions similarly and simultaneously prepared. This method serves to determine 0.02-8.0 mg. of silicon with an error of about 3-5 per cent.

Byall and Ambler⁶⁰ have recommended a procedure, based upon the Briggs modification of the Bell-Doisy method, for the determination of phosphorus and

silica in sugar. The total phosphorus and silica are determined together, and the total phosphorus is then determined alone. Silica is obtained by difference.

(a) Determination of phosphorus and silica.

Reagents. Hydroquinone solution. Dissolve 0.5 g. of hydroquinone in 100 ml. of water containing 1 drop of concentrated sulfuric acid.

Ammonium molybdate solution: Dissolve 25 g. of ammonium molybdate in 300 ml. of water and mix with 200 ml. of water containing 75 ml. of concentrated sulfuric acid.

Standard phosphorus solution: Dissolve 0.4394 g. of monopotassium phosphate in water and dilute to 1 liter. Dilute 25 ml. of this solution to 200 ml. One ml. of this solution contains 0.0287 mg. of P_2O_5 , and is equivalent to 0.0363 mg. of silica.

Procedure. Mix 5 g. of sugar with 0.2 g. of sodium and potassium carbonate in a platinum dish which has been freshly cleared by carbonate fusion. Char carefully until a white ash is obtained. Then heat in an electric muffle at $550^{\circ}C$. and finally over a free flame until a clear melt is obtained. Allow to cool and dissolve in 15 ml. of distilled water. Add 1 ml. of 1:4 acetic acid to neutralize the carbonates and transfer to a tube without filtering. Add 5 ml. of ammonium molybdate reagent and mix well and then add 1 ml. of a freshly prepared 20 per cent sodium sulfite solution. Again mix and add 1 ml. of hydroquinone reagent. Mix and dilute to 100 ml. Again mix and allow to stand for 30 minutes and compare with standards prepared from 0.1 to 4.0 ml. of the standard phosphate solution.

(b) Determination of total phosphorus.

Procedure. Mix 5 g. of sugar in a platinum dish with 0.2 g. of anhydrous sodium and potassium carbonates. Char carefully over a free flame and then incinerate in an electric muffle at a temperature below which the ash fuses. Cool, dissolve the ash in 1 ml. of 1:1 nitric acid and evaporate to dryness on a steam bath. Add 0.5 ml. of concentrated nitric acid and again evaporate to dryness on a steam bath. Treat the residue with 5 ml. of water and immediately filter to remove silica. Collect the filtrate in a 100 ml. Nessler tube and wash the filter until free of acid. Treat the filtrate and washings as described in the foregoing procedure for silica and phosphorus.

(c) Determination of silica. The weight of silica present in the sugar sample can be determined by subtracting the weight of the total phosphorus from the weight of phosphorus and silica.

Pavelka and Morth⁶⁸ used a somewhat similar method for the determination of silicon in pure aluminum.

Mayrhofer and co-workers⁶⁹ used hydroquinone in an indirect method for the determination of small quantities of fluorine in plant and animal materials. The method consists of treating the material containing fluoride with powdered

glass and sulfuric acid and heating. The fluoride is converted into volatile silicon tetrafluoride and is absorbed in a solution of sodium hydroxide. The silicon in this solution is then determined colorimetrically with ammonium molybdate, hydroquinone and a carbonate-sulfite mixture, as described in the foregoing procedure.

Determination of arsenic. Arsenic can be determined in a manner similar to that used for phosphorus, by reducing the arsenomolybdate complex with hydroquinone.⁷⁰

Detection of arsenic. Arsenic can be detected by the yellow coloration which it gives with hydroquinone.⁷¹

Detection of titanium. A solution of hydroquinone in concentrated sulfuric acid gives a crimson color with titanium salts. This reaction is sensitive to 0.1 mg. of TiO_2 , but is not satisfactory for a colorimetric determination.^{72,73,74}

Detection and determination of tungsten. Hydroquinone and tungstic acid dissolved in concentrated sulfuric acid react to give a red color. This reaction was observed by Defacqz⁷⁵ and was used by Heyne^{76,77} for the colorimetric determination of tungsten. The color is dulled somewhat if moisture is present. Small quantities of alkalis, phosphates and nickel have no effect, but nitrate, ferric iron, titanium, columbium, chromate, perhenate and molybdenum interfere. The test fails in the presence of molybdenum, since molybdates also give a color reaction with hydroquinone. The following procedure gives results which are accurate to 10-20 per cent:

Reagents. *Hydroquinone:* Dissolve 10 g. of hydroquinone in 100 ml. of concentrated sulfuric acid.

Standard tungsten solution: Dissolve 63 mg. of pure tungstic oxide in 25 ml. of 10 per cent potassium hydroxide solution and evaporate to dryness. Dissolve the residue in 10 ml. of concentrated sulfuric acid and dilute to 50 ml. with concentrated sulfuric acid. One ml. of this solution contains 1 mg. of tungsten.

Procedure. To a slightly alkaline tungsten solution, add 0.5 ml. of a 10 per cent solution of potassium hydroxide and evaporate to dryness. Add 0.5 ml. of concentrated sulfuric acid and heat until fumes of sulfur trioxide are evolved. Add a few crystals of potassium persulfate to dissolve any organic matter and heat until gases are no longer evolved. Cool the yellow solution in a desiccator.

When cool add 1 ml. of the hydroquinone reagent and dilute to a suitable volume with concentrated sulfuric acid. Compare the resulting red solution with standards similarly treated. Standards for comparison are prepared by diluting 0.1 ml. of the standard solution with 0.5 ml. of a solution of 16 g. of potassium sulfate in 90 ml. of concentrated sulfuric acid. To this add 1 ml. of hydroquinone reagent and dilute to a suitable volume with concentrated sulfuric acid. Both standards and unknown must be protected from the absorption of moisture.

Bogatzki⁷⁸ and Klinger and co-workers⁷⁹ have used hydroquinone for the determination of tungsten in iron and steel. In these procedures the disturbing effects of ferric iron and molybdenum are prevented by the addition of a reducing agent. The procedure described by Bogatzki may be used for determining tungsten in high-speed steels containing chromium. Titanium gives the same color effect as tungsten. The results observed agree closely with those obtained gravimetrically. Klinger and co-workers⁷⁹ claim that the method is reliable only if more than 1 per cent of tungsten is present.

Detection and determination of gold. Hydroquinone, like many other reducing agents, reacts with solutions of gold salts to form colored colloidal solutions of metallic gold. Lenher⁸⁰ observed that gold chloride is instantly reduced with hydroquinone, and Saul⁸¹ used a 0.1 per cent solution of hydroquinone to detect as little as 0.02 per cent gold chloride. A violet colored colloidal solution is obtained in this test. Costeanu^{82,83} has used this reaction for a semi-quantitative test for gold. Spot tests are carried out by impregnating filter paper with a solution of hydroquinone and comparing the spot obtained with the unknown with similar spots prepared using solutions of different but known gold content. Baudisch⁸⁴ has also used hydroquinone as a reagent for gold.

Beamish and co-workers⁸⁵ have found that a 1 per cent solution of hydroquinone causes rapid and complete precipitation of gold from solutions which are 1.2 N in hydrochloric acid. The precipitation of 30 mg. of gold is complete within 2 hours in a cold solution, and under these conditions practically no platinum or palladium is precipitated with the gold. The presence of copper, nickel and zinc is not harmful. Seath and Beamish⁸⁶ have found that gold can be quantitatively separated from tellurium and selenium by precipitating with hydroquinone in a solution which is 1.2 N in hydrochloric acid.

Ryabchikov and Knyazheva⁸⁷ have used hydroquinone for the potentiometric titration of gold.

Procedure. Dissolve the gold in aqua regia, and after adding two times as much sodium chloride to form NaAuCl_4 , treat the mixture in the usual manner to remove the excess nitric and hydrochloric acids. Dilute the solution and determine the gold potentiometrically in a current of carbon dioxide, using a gold wire electrode and slowly adding the hydroquinone solution until a sharp break in potential occurs. Results are improved by heating the mixture to 60-70° C. and acidifying with 5 ml. of 1:4 hydrochloric acid for each 200 ml. of solution. If gold is deposited in a colloidal form, hydroquinone probably has been reduced further than quinone and the results must be discarded. Metallic gold is observed after approximately two thirds of the necessary reagent has been added.

Iridium is the only member of the platinum group which interferes with this determination. The precipitated gold can be titrated with a potassium permanganate solution and iridium determined by difference. Zvyagintsev⁸⁸ has used a similar procedure for the titration of gold in cyanide solutions containing not less than 0.0002 per cent gold:

Procedure. To 100 ml. of cyanide solution, add 5-10 ml. of nitric acid and heat to boiling. Add 1-1.5 g. of potassium chloride in small portions during a period of 15-20 minutes, and boil the solution for 30 minutes. Cool, add sodium or potassium hydroxide until the mixture is weakly acid to litmus and determine the gold content by titrating with hydroquinone.

Pollard⁸⁹ has used hydroquinone for the rapid volumetric assay of gold.

Detection and determination of silver. Silver may be detected, and approximately determined by the stains formed when a solution of a silver salt is added to paper which has been impregnated with a saturated solution of hydroquinone.⁹⁰ By using drops of silver solutions of known but different silver content so as to form a comparison series, the approximate silver content of a drop of unknown solution can be determined.

Detection of rhenium. Heyne and Moers⁹¹ have used hydroquinone for the detection of rhenium salts. Rhenium salts react with hydroquinone in concentrated hydrochloric acid to give brown and green colors. Wenger and Duckert,⁹² who have reviewed the various reactions for rhenium, state that hydroquinone is neither sensitive nor specific, and is not to be regarded as a satisfactory reagent for rhenium.

Determination of copper. Small quantities of copper may be determined colorimetrically with hydroquinone after a preliminary electrolytic separation. The copper deposit is dissolved in dilute acid, the resulting solution evaporated to dryness, and the residue is then dissolved in 1 ml. of 0.001 N hydrochloric acid. Copper is finally estimated by measuring the blue color which is formed when this solution is treated with a little sodium hydroxide and hydroquinone. Good results are claimed with quantities of copper ranging from 0.004 to 0.095 mg.¹⁰²

Detection of copper. A dilute aqueous solution of hydroquinone is colored blue in the presence of a trace of cupric ion. The reaction proceeds more rapidly if the solution is heated to boiling. Aloy and Valdiguié⁹³ report that this reaction is more sensitive than the blue color with ammonium hydroxide or the pink color with ferrocyanide. They recommend as a reagent a 0.2 per cent aqueous solution of hydroquinone, and state that the solution to be tested should be neutral or only slightly acid, and should contain no considerable quantity of any salt.

Determination of iron. Cowling and Benne⁹⁴ suggest the use of ammonium citrate to prevent interference by aluminum in the determination of iron with 1,10-phenanthroline. They have found that hydroquinone is a more satisfactory reducing agent for ferric iron than hydroxylamine hydrochloride in the presence of ammonium citrate.

Separation of selenium from metals. In the analysis of native selenides, it is often necessary to separate selenium from accompanying metals. By the action of reducing agents in strongly alkaline solutions it is possible in some instances to precipitate the metal and leave selenium dioxide in solution. Geilmann and Wrigge⁹⁵ have used this reaction for the separation of selenium from copper, bismuth, mercury and silver in the selenides of these metals alone or in

metals with gold and platinum. Iron, calcium and magnesium do not interfere. Lead selenide cannot be analyzed in this way, since much lead passes into the alkaline solution. Selenium dioxide in the filtrate can be precipitated by acidifying with concentrated hydrochloric acid and treating with sulfurous acid.

A suitable reducing agent is prepared by dissolving 15 g. of hydroquinone and 80 g. of sodium sulfite in 500 ml. of water. This solution is mixed when needed with suitable portions of a solution containing 100 g. of sodium hydroxide in 500 ml. of water.

Detection of nitrite. A solution of hydroquinone in 50 per cent acetic acid gives an intense yellow coloration with nitrites, but the reaction will not detect less than 1 mg. of N_2O_3 per liter.⁹⁶

Detection and determination of nitrates. Quinolic or phenolic compounds, when dissolved in concentrated sulfuric acid, give color reactions with alkali nitrates. Eitel⁹⁷ recommends hydroquinone for the detection of small quantities of nitrate when nitrites are present, but considerable quantities of halides must be absent. Bini^{98,99} recommends the use of hydroquinone for the preparation of hydroquinonesulfonic acid, which is used for the determination of small quantities of nitrates (page 251).

Detection of alkalinity in solid salts. Maldiney¹⁰⁰ has reported that blue and gray colors are obtained when solid hydroquinone is mixed with solid alkali carbonates. This effect has been attributed to the action of light and slight oxidation of the reagent, but French and Saunders¹⁰¹ have shown that the reaction depends upon the presence of a slight amount of moisture. Only the more alkaline salts give similar colors. These range from gray through green and blue to black, and are roughly proportional to the increasing alkalinity of the compound. In this way the approximate alkalinity of a solid sample can be determined. For example, it is possible to distinguish between tri- and diphosphates, since the latter give no color with hydroquinone. Similarly it is possible to distinguish between tri- and di-arsenates and between normal carbonates and bicarbonates.

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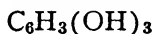
HYDROXYHYDROQUINONE

Synonym: 1,2,4-Trihydroxybenzene



Mol. Wt. 126.11

Beil. Ref. VI, 1087.



Use: Detection of cerium, copper, hypiodite, iodate, iron, mercury, silver and vanadium.

Determination of gold.

Hydroxyhydroquinone is a bluish-green to gray crystalline solid which melts at 134-135° C. It dissolves readily in water to form a brown solution. It is also

soluble in alcohol and ether but is almost insoluble in chloroform, benzene and carbon disulfide. The reagent is sensitive to oxidation.

Preparation. Add 150 g. of quinone to a mixture of 400-450 g. acetic anhydride and 10 ml. of concentrated sulfuric acid. Keep the temperature at 40-50° C. and pour, when all the quinone is dissolved, into a large quantity of water. The triacetate precipitates as an oil which rapidly solidifies. Boil 50 g. of the triacetate for 1 hour with 100 ml. of methyl alcohol and 10 ml. of sulfuric acid. Neutralize the acid with an equivalent quantity of anhydrous sodium carbonate. Mix with ether, filter off the sodium sulfate, and evaporate the ether and methyl alcohol on a water bath. Crystallize the residue in a vacuum desiccator.¹

Reactions with metals. Ferrous salts react with hydroxyhydroquinone to give a greenish-blue color, whereas ferric salts give a gray-blue color. Ceric compounds give an intense red color. Antimony and bismuth do not react, and in this respect hydroxyhydroquinone differs from pyrogallol. Copper, silver, gold, mercury and vanadium salts are reduced to the metal. Tetravalent lead is reduced to the bivalent state. Hypiodites and iodates in an alkaline medium give a carmine-red coloration.² Beamish and co-workers³ report that gold is quantitatively reduced to the metal by hydroxyhydroquinone.

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METHYLPYROCATECHOL Synonym: 1-methyl-3,4-dihydroxybenzene

$C_7H_8O_2$

Mol. Wt. 124.13

Beil. Ref. VI, 878.

$CH_3-C_6H_3(OH)_2$

Use: Detection of nitrite.

Methylpyrocatechol is a solid melting at 65° C. and boiling at 251-252° C. It is soluble in water, alcohol and ether.

Detection of nitrite. Nitrite may be detected by the wine-red color which is obtained in a reaction with methylpyrocatechol. The color is obtained by adding methylpyrocatechol to the solution of nitrite, making alkaline with sodium hydroxide and heating. This reaction is sensitive to 1 part of nitrite in 1,000,000 parts of solution.^{1,2}

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α -NAPHTHOL

Synonym: α -Hydroxynaphthalene

$C_{10}H_8O$

Mol. Wt. 144.16

Beil. Ref. VI, 596.

$C_{10}H_7OH$

Use: Detection of columbium, copper, germanium, nitrite, titanium, tungsten and vanadium.

Determination of nitrite.

α -Naphthol is a colorless solid possessing a phenolic odor. It melts at 96° C. and boils at 278°-280° C. It is sublimable and is volatile in steam. It darkens on exposure to light. The compound is only slightly soluble in water but dissolves readily in alcohol, benzene, chloroform, ether and solutions of alkali hydroxides.

Preparation. α -Naphthol is prepared by fusing the sodium salt of α -naphthalenesulfonic acid with sodium hydroxide. α -Naphthalene sulfonic acid is mixed with three times as much sodium hydroxide and heated at 300-320° C. until the mixture separates into two layers. The upper layer is the sodium salt of α -naphthol. Dissolve in water and precipitate α -naphthol by the addition of an acid. Purify by distillation.^{1,2}

Detection of tungsten, columbium and titanium. Tungsten may be detected with α -naphthol by means of the following procedure.³

Procedure. Convert the tungsten compound to tungstic acid and heat with 4-5 times its weight of potassium bisulfate and a few drops of sulfuric acid. Mix with sufficient concentrated sulfuric acid to prevent solidification on cooling and add a little α -naphthol. A violet color is formed if tungsten is present.

Columbium, tungsten and titanium may also be detected by color reactions which are obtained with the double fluorides of these metals and α -naphthol. The test is carried out by dissolving a little α -naphthol in 8-10 drops of concentrated sulfuric acid and adding a few crystals of the double fluoride. A faint yellow color is obtained with columbium; a green to dark greenish-brown color with tungsten; and deep blue color with titanium.^{4,5} The latter is a sensitive test.

Detection of vanadium. Several tests for vanadium have been proposed which depend upon the catalysis of oxidation reactions by this metal. The following test includes the use of α -naphthol:⁶

Procedure. To the solution to be tested add 1 ml. of 0.1 per cent α -naphthol, 1 ml. of 0.1 per cent *p*-phenylenediamine and 1 ml. of a saturated solution of potassium chlorate. Dilute to 5 ml. Prepare a second solution exactly like the first except that a volume of distilled water equal to that of the unknown is used. Place both the blank and the solution to be tested in a water bath for 1 minute. A brownish-red color is obtained with as little as 0.1% of vanadium. Tin interferes but may be eliminated by addition of potassium oxalate. Silver also interferes but can be removed with sodium chloride. Lead must be absent.

Detection of germanium. α -Naphthol is used with phthalic acid for the preparation of hydroxynaphthalenequinonesulfonic acid reagent, which is used for the detection of germanic acid (page 210).⁷

Detection of copper. When added to a dilute solution of a cupric salt, α -naphthol gives a characteristic blue-violet coloration which can be used to detect very small quantities of copper.⁸

Procedure. Add 0.2 g. of α -naphthol to 100 ml. of water to which 20 drops of 0.01 N hydrochloric acid have been added, and heat 10 ml. of this solution

for 20-30 seconds in a boiling water bath. Add 1-2 drops of the dilute solution to be tested. A blue color indicates the presence of copper.

Detection and determination of nitrite. α -Naphthol is frequently used with sulfanilic acid and other amines for the detection of nitrites.⁹ Zambelli^{10,11} originally proposed the following test for nitrite in water :

Procedure. Add a solution of sulfanilic acid in dilute sulfuric acid to 200 ml. of water to be tested. After 10 minutes add a little aqueous solution of α -naphthol and make alkaline with ammonium hydroxide. A rose to deep red color is obtained if nitrite is present. This reaction will detect 1 part of nitrous acid in 25,000,000 parts of water.

Modifications of this reaction have been used by Vagi¹² and De Paepe.¹³

Sulfuric acid containing the oxides of nitrogen gives a green color with α -naphthol. This test is more sensitive in the presence of sucrose, which makes possible the detection of as little as 5 p.p.m. of the oxides of nitrogen :¹¹

Procedure. Mix 1 ml. of 0.1 per cent sucrose solution in water with 0.5 ml. of a 5 per cent alcoholic solution of α -naphthol, and add 2 ml. of the solution to be tested. A violet-ring at the interface of the liquids is a test for carbohydrates (Molisch), and the lower layer is green or yellow if the oxides of nitrogen are present.

Chromates and molybdic acid interfere, but bromide, chloride, sulfite, thio-sulfate, acetate, borate, chlorate, phosphate, sulfide, barium, strontium, calcium, copper, cadmium, zinc, mercury, lead, manganese, and magnesium do not interfere.

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β -NAPHTHOL

Synonym : Betanaphthol, β -hydroxynaphthalene

$C_{10}H_8O$

Mol. Wt. 144.16

Beil. Ref. VI, 627.

$C_{10}H_7OH$

Use: Detection of bromine, chlorine, chlorate, columbium, copper, nitrite, titanium and tungsten. Determination of carbon monoxide, copper, nitrite and potassium.

β -Naphthol consists of pale, buff-colored crystals or of a white to yellowish-white crystalline powder. It has a slight phenolic odor and darkens upon standing and on exposure to light. It sublimes when heated and may be distilled in vacuo. It melts at 122-123° C. and boils at 285-286° C. One gram of the solid dissolves in a liter of water, 0.8 ml. of alcohol, 17 ml. of chloroform and 1.3 ml. of ether.

Preparation. β -naphthol is prepared by fusing 30 g. of β -naphthalene sodium sulfonate with 90 g. of sodium hydroxide and 3 ml. of water. The water and sodium hydroxide are heated to 280° C. in a nickel crucible and then the powdered naphthalene sulfonate is added in small portions. When all the reagent is added, heat to 310-320° C. and maintain at that temperature for a few minutes until the yellow mass becomes less viscous and darker in color and separates into two layers. Allow to cool and dissolve the cold product in a little water and acidify with a mixture of equal volumes of hydrochloric acid and water. Filter off β -naphthol when cool and recrystallize from water.^{1,2}

Detection and determination of nitrite. Nitrites are frequently detected by reactions based upon the formation of diazo compounds and subsequent coupling of these substances with various amines and phenols to yield colored dye molecules. β -naphthol is frequently employed as a coupling agent in these reactions. Eegriwe,³ for example, has used β -naphthol with benzidine in a test based upon this principle:

Procedure. Acidify the solution to be tested with dilute sulfuric acid and hold above this mixture a stirring rod moistened with a 1 per cent solution of benzidine hydrochloride. Place the stirring rod in a test tube and add a drop of 0.04 per cent β -naphthol solution, mix and add a drop of ammonium hydroxide. A violet-red color appears if nitrite is present. By this test, 0.004 mg. of nitrite can be detected in 5 ml. of solution.

A similar test has been used by Bittencourt and Barreto.⁴ Alzamora⁵ has used β -naphthol in conjunction with xylidine acetate for the detection of nitrite:

Reagents. *Xylidine acetate solution:* Dissolve 1.81 g. of xylidine acetate in 10 ml. of acetic acid and sufficient water to make 1 liter of solution.

β -Naphthol solution: Dissolve 2.65 g. of β -naphthol and 10 g. of sodium hydroxide and dilute with water to 1 liter.

Procedure. Place 50 ml. of the solution to be tested in a Nessler tube and add 1 ml. of the xylidine acetate solution. Shake well and allow to stand for 5 minutes, and add 5 ml. of the β -naphthol solution. An orange-red color is formed which is suitable for the detection and determination of nitrite. This reaction is sensitive to about 0.003 mg. of sodium nitrite per ml. of solution.

Riegler and others^{6,7,8} have used β -naphthol and sodium naphthionate for the detection of nitrite.

Reagent. Shake vigorously 2 g. of sodium naphthionate and 1 g. of β -naphthol with 200 ml. of water and filter.

Procedure. Add 10 drops of the reagent and 2 drops of hydrochloric acid to 10 ml. of the solution to be tested and shake vigorously. Carefully add 20 drops of ammonium hydroxide. A reddish ring forms at the junction of the two liquids, and on shaking the solution becomes rose to red in color. This reaction will detect 1 part of nitrite in 10,000,000 parts of solution.

α -Naphthol may also be coupled with diazotized sulfanilic acid for the detection of nitrite,^{9,10} but this is generally less satisfactory than β -naphthol.¹⁰

Hager¹² has used a 1 per cent solution of β -naphthol in alcohol to detect nitrites and nitrates. A yellow to dark cherry-red color is obtained with solutions of nitrites or nitrates in concentrated sulfuric acid.

Determination of potassium. Potassium may be determined indirectly by a method proposed by Tischer.^{13,14,15} Potassium is precipitated as the cobalt-nitrite, and the nitrite content of the precipitate is determined by the method of Riegler (page 143), using a reagent consisting of 5 g. of sodium naphthionate and 2.5 g. of β -naphthol in 500 ml. of water.

Detection and determination of copper. Copper reacts with β -naphthol to give a color varying from yellow to blue. This method was used by Fulton¹⁶ for the detection of copper, and was suggested by Snell¹⁷ as a possible method for the colorimetric determination of copper. The test is carried out as follows:

Procedure. Dissolve 0.04 g. of β -naphthol in 2 ml. of alcohol, add 0.5 ml. of 6 N ammonium hydroxide and immediately add 5 ml. of the solution to be tested. An ammoniacal solution of β -naphthol in alcohol has a light pink color, but in the presence of copper this changes to a cloudy yellowish-green. The reaction will detect 1 part of copper in 3 million parts of solution.

Muller and Burtzell¹⁸ state that the colorimetric determination of copper based on this reaction is less satisfactory than that employing salicylic acid or carbamate.

Detection of columbium, tungsten and titanium. β -Naphthol may be used in a color reaction for tungsten. The tungsten compound is converted to tungstic acid and heated with 4-5 times its weight of potassium acid sulfate and a few drops of sulfuric acid. Sufficient concentrated sulfuric acid is then added to prevent solidification on cooling, and the resulting liquid is treated with a little β -naphthol. A violet-blue color is formed with tungsten.¹⁵

β -Naphthol also reacts with the double fluoride of columbium, titanium and tungsten.²⁰

Procedure. Dissolve a little β -naphthol in 8-10 drops of concentrated sulfuric acid in a porcelain dish and add a crystal of the double fluoride. A faint yellowish-brown is obtained with columbium; a delicate coffee-brown color with tungsten; and a brown color, eventually changing to dark blue with titanium.

Detection of chlorate. Alvarez^{21,22,23,24} has used β -naphthol for the detection of chlorates.

Reagent. Mix 0.1 g. of β -naphthol with 0.01 g. of diphenylamine and 10 ml. of sulfuric acid.

Procedure. Place approximately 1.0 mg. of the salt suspected of being a chlorite on a porcelain plate and pour over this 5-6 drops of the reagent. A dull green color appears which in time becomes almost black.

Determination of carbon monoxide. A suspension of cuprous oxide in sulfuric acid containing β -naphthol^{25,26} may be used for the absorption of carbon monoxide in gas analysis. According to LeBeau and Bedel^{27,28} this reagent is more effective at 60° C. than at room temperature. Complete absorption occurs within 3 minutes.

Detection of chlorine and bromine. The following test has been used by Hager^{29,30} for the detection of free chlorine or bromide.

Procedure. Superimpose 0.5 ml. of a 1 per cent alcoholic solution of β -naphthol on the surface of 4-5 ml. of the solution to be tested and allow the mixture to stand for a few minutes. A milky ring forms at the junction of the two liquids if chlorine or bromine is present.

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ORCINOL Synonym: Orcin, 3,5-dihydroxytoluene, 5-methylresorcinol
 $C_7H_8O_2$ Mol. Wt. 124.13 Beil. Ref. VI, 882.
 $CH_3-C_6H_3(OH)_2$

Use: Detection of antimony, chromium, nitrate, nitrite and nitrosyl sulfuric acid.

This compound occurs as white crystals, which have a sweet but unpleasant taste. These crystals redden when exposed to air due to oxidation. The melting point is $107^\circ C$. The boiling point is $290^\circ C$. The compound is soluble in water, alcohol, and ether, but is less soluble in benzene, and only slightly soluble in chloroform or carbon disulfide.

Preparation: Orcinol is prepared by heating the alkali salt of toluene-m-disulfonic acid with sodium hydroxide to $280^\circ-320^\circ C$.¹

Detection of nitrite, nitrate, and nitrosyl sulfuric acid. Vagi² reports that a solution prepared by dissolving 1 g. of orcinol in 300 ml. of 50 per cent acetic acid is a good reagent for detecting nitrites. An intense yellow coloration is produced when the reagent is added to a solution containing 1-5 mg. of N_2O_3 per liter. By treating a nitrite or nitrate with concentrated sulfuric acid, nitrosyl sulfuric acid is formed, and this compound yields strongly colored compounds with phenols. Eichler³ has used orcinol for this reaction, although resorcinol is more commonly used. For details of the test, see the section on resorcinol (page 181).

Detection of chromates. An alcoholic solution of orcinol gives a brown color with chromates. This reaction has been used by Gutzeit⁴ as a test for chromates.

Detection of antimony pentachloride. Orcinol, like other phenols, gives a color reaction with antimony pentachloride.⁵

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PHENOL Synonym: Carboic acid
 C_6H_6O Mol. Wt. 94.11 Beil. Ref. VI, 113.
 C_6H_5OH

Use: Detection of ammonia, antimony, arsenic, bismuth, columbium, copper, hydrogen peroxide, nitrate, nitrite, tantalum, tin, titanium, vanadium and water.

Determination of ammonia, barium, calcium, gold, halogens and halogen acids, magnesium, nitrate, nitrite, potassium and strontium.

Phenol consists of acicular crystals or a white crystalline mass which possesses a characteristic odor. It is poisonous and caustic. The compound may become reddish upon exposure to air and light, and this action is hastened in the presence of alkalis. When free from water and cresols phenol solidifies at 41°C . and melts at 43°C . It boils at 182°C . The compound is liquefied when mixed with about 8 per cent of water. One gram of the solid dissolves in 15 ml. of water and 12 ml. of benzene. It is very soluble in alcohol, chloroform, ether, glycerol and carbon disulfide.

Detection and determination of nitrites and nitrates. Highly characteristic colored products are formed when nitrites and nitrates are mixed with some phenols in the presence of concentrated sulfuric acid. Sprengel¹ has proposed the use of phenol with sulfuric acid as a test for nitrates. Similar tests which have been proposed by Fresenius² and others³⁻⁶ do not distinguish between nitrates and nitrites. The test may be applied to a dry residue of the salts to be tested. The following method has been suggested by Lindo⁷:

Reagent. Place 10 mg. of phenol in a 100 ml. flask, add a little water, 25 ml. of alcohol and dilute to the mark with water.

Procedure. Add 1 drop of the above reagent to 0.5 ml. of the solution to be tested and carefully underlay with 2 ml. of concentrated sulfuric acid. Color reactions are obtained with nitrites as follows:

Concentration of N_2O_5	Color Reaction
1:200,000	Faint pink band with faint green color below
1:50,000	Red and green bands
1:2,000	Intense red and green color

With nitrates the following color reactions are obtained:

Concentration of N_2O_5	Color Reaction
1:20,000	Faint yellow
1:10,000	Faint orange
1:1,000	Intense orange

In the presence of chlorides, nitrates yield a reddish solution when treated with phenol and sulfuric acid. This color changes to blue when neutralized with an excess of ammonia. This reaction is sensitive to one part of nitrate in 4,000,000 parts of water. The reaction may be used for the colorimetric deter-

mination of nitrates.^{8,9} Zambelli^{10,11} has substituted phenol for α -naphthol as a coupling agent in the well-known reaction with sulfanilic acid for nitrites. A red color is obtained with α -naphthol, but with phenol the color of the resulting dye is yellow. Frankland¹² prefers the Zambelli modification of the nitrite test to the sulfanilic acid-naphthylamine hydrochloride and m-phenylenediamine procedures. Lombard¹³ has used this reaction as follows:

Reagent. Dissolve 1 g. of sulfanilic acid in 100 ml. of saturated aqueous ammonium chloride solution with the aid of heat and add 1.5 g. of phenol. Mix with 100 ml. of 2 N hydrochloric acid.

Procedure. Add 1 ml. of the reagent to 50 ml. of the solution to be examined, allow to stand for 5 minutes, and add 1 ml. of ammonium hydroxide with shaking. A yellow color forms if nitrites are present.

Stone^{14,15} has based a test for nitrites upon the deep yellow color which is formed when aniline and phenol are added to a solution containing nitrite.

Reagent. Mix 1 g. of phenol, 1 ml. of aniline and 15 ml. of concentrated hydrochloric acid with 150 ml. of water.

Procedure. Neutralize the solution to be tested and add 0.5 ml. of the reagent. Make alkaline with sodium hydroxide. A deep yellow color appears if nitrite is present.

The most important use of phenol in the determination of nitrates is based upon its conversion to phenolsulfonic acid by treating with sulfuric acid. For a discussion of this application, see section on phenolsulfonic acid (page 255). Many dyes may be coupled with phenol in the nitrite test.¹⁶

Phenol may also be used in the determination of nitrates by means of the Kjeldahl method. If 0.2 g. of an alkali nitrate is treated with 1 g. of phenol in 20 ml. of concentrated sulfuric acid and 10 g. of potassium sulfate and then heated, the conversion of nitrate into ammonium bisulfate is usually incomplete. If the potassium sulfate is not added at the start, but the reaction is allowed to proceed in the cold for some time and the potassium sulfate added only after heating for an hour or more, the results are said to be quantitative.¹⁷

Determination of potassium. Potassium may be determined colorimetrically by a method which depends upon the precipitation of potassium as $K_2NaCo(NO_2)_6$, and the determination of the nitrite content of the precipitate by means of the formation of the yellow azo dye, tropeolin.^{13,18}

Reagents. *Phenol-sulfanilic acid reagent.* Dissolve 1 g. of sulfanilic acid in 100 ml. of hot saturated ammonium chloride solution, and mix with 1.5 g. of phenol in 100 ml. of water.

Sodium cobaltinitrite reagent. Dissolve 25 g. of cobalt nitrate in 50 ml. of water and 12.5 ml. of acetic acid. Prepare a second solution by dissolving 120 g. of sodium nitrite with warming in 180 ml. of water. Mix 1 part of the cobalt nitrate solution with 3 parts of the sodium nitrite solution and allow to stand for 5 hours. Filter and use the filtrate as the reagent.

Procedure. Place exactly 1 ml. of a solution containing 0.025-0.1 mg. of K_2O in a centrifuge tube, acidify with 1-2 drops of 3 N acetic acid, and treat with 1 ml. of sodium cobaltinitrite reagent. Shake well, allow to stand 4 hours, and centrifuge for 15 minutes at 2-3000 r.p.m. Remove the supernatant liquid, wash with 2 ml. portions of water, and 5-6 minutes rotation in the centrifuge until a perfectly clear wash liquid is obtained. Dissolve the precipitate in 5 ml. of 0.1 N sodium hydroxide solution, and heat in a water bath. Disregard any cobalt hydroxide which forms. Transfer the alkaline solution to a 100-ml. volumetric flask and dilute with 50-60 ml. of water. Mix with 2 ml. of a mixture of equal parts of 10 per cent hydrochloric acid and the phenol-sulfanilic acid solution. Mix well, and allow to stand for 15 minutes. Make the solution alkaline with 10 per cent ammonia and dilute with water to 100 ml. Compare the color of 15-30 ml. of this solution with colors produced similarly with known quantities of nitrite solution.

Since the composition of the precipitate does not correspond exactly to $K_2NaCo(NO_2)_6$, it is important that the conditions are absolutely the same for the preparation of the standard solution and the unknown.

Detection and determination of ammonia. Thomas¹⁹ has based a method for the detection and determination of ammonia upon the intense blue color which is formed by the reaction of an ammonium salt with phenol and sodium hypochlorite. This reaction is said to be about equal in sensitivity to the well-known Nessler reaction, but according to Foxwell²⁰ is not as accurate as the distillation method.

The following procedure for the estimation of ammonia is given by Foxwell²⁰:

Procedure. Prepare a standard by dissolving 0.063 g. of pure ammonium chloride in water and diluting to 1 liter. Use a buret and add quantities of this solution ranging from 0.1 to 5 ml. into 13 test tubes of equal internal diameter. Dilute each sample to 5 ml. with water, add 1 ml. of a 4 per cent phenol solution and 1 ml. of a dilute solution of sodium hypochlorite. Immerse these tubes in boiling water for at least 90 seconds to develop the blue color.

To test a sample of waste liquor for total ammonia, dilute 5 ml. to 300 ml. with water, pipet 5 ml. of this solution into a test tube which is similar to those employed above, add 1 ml. of 4 per cent phenol solution and 1 ml. of sodium hypochlorite. Heat as described above, cool and compare with standards.

To determine fixed ammonia, boil 5 ml. of the waste liquor, to expel free ammonia, dilute to 300 ml. and proceed as described above.

The test should not be carried out in the presence of free acids, although free calcium oxide is without effect. The foregoing method is sufficiently accurate for control purposes. Orr^{21,22} has used a similar reaction for the colorimetric estimation of ammonia in urine.

A qualitative test may be carried out in a manner similar to that described above. A distinct coloration is obtained with 0.0001 mg. of ammonia. Crismer²³ has used such a method for the photometric determination of ammonia. Ammonia is first separated by the method of Conway and Byrne,²⁴ and is then

treated with phenol and sodium hypochlorite, as in the method described by Berthelot, or by a new and improved method based upon the use of phenol and chloramine T. The resulting blue color is compared with a standard in a Pulfrich photometer.

Karaoglanov²⁵ has recently studied various methods which have been proposed for the detection of ammonia, and reports that the most sensitive are those using sodium chloride and mercuric chloride, and phenol and sodium hypochlorite. By the latter method as little as 1 γ of ammonia in 10 ml. of solution can be detected.

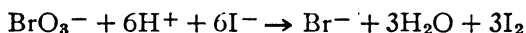
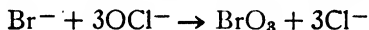
Detection and determination of halogens. Phenol has been used in many analytical procedures applying to the detection and the determination of the halogens. Many of these reactions are based upon the use of phenol for the elimination of excess halogens. Wandenblucke²⁶ has used phenol in a procedure for the titration of hypochlorites. This method is based upon the fact that 1 mole of sodium hydroxide is liberated for every mole of hypochlorite which reacts with phenol. The original alkalinity of a hypochlorite solution can be determined by destroying the active chlorine in a known quantity of solution with hydrogen peroxide, which is added until methyl orange is no longer decolorized, and then titrating with 0.1 N sulfuric acid. The same quantity of the hypochlorite solution is then treated with a quantity of phenol which 2-3 times the weight of the hypochlorite present, and after standing for 5 minutes, the alkalinity of the resulting solution is determined by titration with 0.1 N of sulfuric acid, using methyl orange as an indicator. The difference between the two alkalinities, recorded as milligrams of chlorine, gives the amount of chlorine in the solution. This method does not seem to present any particularly desirable features and is much less sensitive than the arsenious acid method.

Schulek²⁷ has used phenol for the determination of iodate in the presence of hypiodite and for bromate in the presence of hypobromite. The determination is based upon the fact that phenol reacts with hypiodous and hypobromous acids but not with iodic or bromic acids. To make the determination, add an excess of 5 per cent phenol solution to the mixture of the oxygen acids and saturate with carbon dioxide. Then add potassium iodide, make acid with sulfuric acid, and titrate with a standard thiosulfate solution.

Szabo^{28,29} has used phenol for the determination of small quantities of bromine:

Procedure. To 10 ml. of a solution containing 0.01-0.35 g. of bromide ion in a 100 ml. beaker add 1 g. of potassium bicarbonate and the necessary volume of freshly prepared chlorine water (4.5-5.0 mg. of chlorine). Evaporate the solution rapidly over a wire gauze and the instant solidification takes place, remove the flame. Dissolve the residue in 20 ml. of water, and add with stirring 5 ml. of 1 per cent phenol solution from a pipet. Allow to stand for 5 minutes, add 2-5 mg. of powdered potassium iodide to the solution and acidify with 5 ml. of 20 per cent sulfuric acid. Again allow to stand for 5 minutes and titrate the liberated iodine with 0.001 N sodium thiosulfate solution, adding starch indicator toward the last.

The previous reaction is based upon the following equation:



Phenol is added to the reaction mixture to remove the excess chlorine.

Lisboa e Costa³⁰ has used phenol for the determination of iodine in aqueous or alcoholic solutions. A 5 per cent phenol solution is added to the mixture to be titrated and the hydrogen iodide formed is titrated with 0.1 N borax.

Bromine is used in many analytical procedures as an oxidizing agent, and phenol is often added to remove the excess bromine before proceeding with other steps of the procedure.^{31,32}

Determination of the alkaline earths. Lindet³³ has proposed the use of phenol in a procedure for the determination of oxides of calcium, strontium and barium in the presence of carbonates and phosphates. The oxides of the alkaline earth metals dissolve in phenol, whereas the carbonates and the phosphates are insoluble. After filtration the oxides of calcium, barium and strontium can be determined in the filtrate by titration with N hydrochloric acid.

Lindet and Brasart³⁴ have recommended the use of phenol to replace sucrose in increasing the solubility of lime. Phenol gives a solution which is easily titrated with N hydrochloric acid and the method is applicable with barium oxide and magnesium oxide.

Detection of copper. Jawarowski^{35,36} observed that when an excess of ammonia and 2 drops of phenol are added to 5 ml. of solution containing a copper salt a blue color develops in about an hour depending on the quantity of copper present.

Fulton³⁷ has modified this reaction as follows:

Procedure. To an alcoholic solution containing phenol, add 0.5 ml. of 3 per cent hydrogen peroxide, 0.5 ml. of 5 N ammonium hydroxide, and 5 ml. of the solution to be tested. A pink to red color forms if copper is present.

This reaction constitutes a general test for phenols, and various phenolic compounds may be used to replace phenol in the foregoing procedure. It is probable that a compound of copper with phenol is formed and that the action is not catalytic as has previously been assumed.

Phenol has been used to eliminate interference by iron in the electrolytic determination of copper.³⁸

Detection of hydrogen peroxide. Spiro³⁹ has used phenol in a sensitive test for hydrogen peroxide:

Procedure. Add a few drops of a solution of 0.1 N hydrogen peroxide and of freshly prepared 0.01 N ferrous sulfate solution to a dilute phenol solution. An intense green color is formed. Upon the addition of dilute ammonium hydroxide, ammonium carbonate, or sodium carbonate this color changes to a reddish-violet. This changes to green upon the addition of acids.

Determination of gold. Beamish and co-workers⁴⁰ have found that gold salts are quantitatively reduced to the metal by phenol.

Detection of columbium, tantalum, titanium, tin, arsenic, vanadium and bismuth. Titanic, tantalic, columbic, stannic, arsenic and vanadic acids and bismuth oxide give various color reactions with alkaloids and phenols in sulfuric acid solutions. These reactions have been used by Levy,⁴¹ Defacqz⁴² and others⁴³⁻⁴⁶ for the detection of the above elements.

Detection of antimony. Ekkert⁴⁷ has used phenol for the detection of antimony pentachloride. Chloroform solutions of antimony pentachloride give color reactions with various phenols, including phenol.

Detection of water. Romei⁴⁸ has used dry potassium phenoxide, for the detection of water in ether. The potassium salt is partially soluble in ether containing water, and the undissolved part is colored reddish-brown. The reagent is almost insoluble in anhydrous ether. According to Romei this reaction may be used to detect 0.25 per cent of water in ether.

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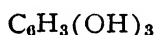
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PHLOROGLUCINOL Synonym: Phloroglucin, 1,3,5-trihydroxybenzene

$C_6H_6O_3$

Mol. Wt. 126.11

Beil. Ref. VI, 1092.



Use: Detection of antimony, arsenic, cerium, chromate, chromium, gold, iron, mercury, nitrite, osmium, palladium, tin and vanadium.

Phloroglucinol consists of white or yellowish crystals which become anhydrous at 110° C. The compound becomes discolored upon standing in light. It melts, when anhydrous, at 216-219° C. when rapidly heated and at about 200° C. when slowly heated. It is soluble in 100 parts of water and 10 parts of alcohol. It is soluble in ether.

Preparation: Add 210 g. (180 ml.) of concentrated hydrochloric acid to 22.5 g. of 2,4,6-trinitrobenzoic acid and then add 83 g. of tin in small portions. The mixture should be contained in a flask equipped with a reflux condenser. After adding a few grams of tin, the reaction is started by immersing the flask in hot water. Add the rest of the tin through the condenser at such rate that the action proceeds fairly rapidly. Finally heat the mixture on a steam bath for about 1 hour to complete the reaction and then remove the tin by filtering while hot through glass wool. Dilute the filtrate to exactly 200 ml., and add 40 per cent sodium hydroxide until a slight permanent precipitate is formed. Then add more 40 per cent sodium hydroxide solution until the mixture is alkaline to litmus. Add to the filtrate 100 g. of cracked ice and sufficient alkali to neutralize the free acid, and then add about 80 ml. of 40 per cent sodium hydroxide. Dilute to about 600 ml. and boil under reflux in an atmosphere of carbon dioxide for about 20 hours. Filter, wash thoroughly with boiling water and concentrate the filtrate by

evaporation. Acidify with hydrochloric acid to litmus, cool to 0° C., and filter. Dissolve in hot water, again filter and crystallize at 0° C.¹

Detection of mercury. Polyphenols with the hydroxy groups in the meta position react with mercuric ions to form difficultly soluble salts. Vesel'skaya² recommends phloroglucinol as the most sensitive of these compounds. By means of this reagent as little as 20γ of mercuric ion per ml. of solution can be detected. Resorcinol and orcinol may also be used but they are less sensitive.

Bromides, chlorides, iodides, cyanides and thiocyanates interfere with this reaction but they can be removed with the aid of silver nitrate. Sodium, potassium, ammonium, calcium, zinc, strontium, chromium, aluminum, antimony, uranyl, manganese, titanium and bismuth salts do not form precipitates with phloroglucinol.

Detection and determination of gold. Phloroglucinol reacts with solutions of gold salts to reduce them quantitatively to metallic gold. This reagent has been suggested as a substitute for hydroquinone in the detection and determination of gold.³

Detection of antimony. Phloroglucinol, like many other phenols, reacts with chloroform solutions of antimony pentachloride to give a color reaction which can be used for the detection of antimony.⁴

Detection of chlorine. Raikow⁵ has used phloroglucinol in the preparation of a reagent for detecting chlorine in benzoic acid.

Reagent. Dissolve 1 g. of vanillin and 1 g. of phloroglucinol in 100 ml. of ether.

Procedure. Allow 0.5 ml. of the solution to evaporate from the porcelain cover of a crucible, and then hold the inverted cover over the flame of an alcohol lamp in which the benzoic acid is ignited on a loop of platinum wire. If chlorine is present, the vanillin-phloroglucinol mixture becomes rose-red to carmine-red.

Detection of hydrochloric acid. Gunzberg⁶ has used phloroglucinol in a reagent for the detection of free hydrochloric acid in gastric juice.^{7,8,9}

Procedure. The reagent is a solution of 2 g. of phloroglucinol and 1 g. of vanillin in 40 ml. of alcohol. Mix equal volumes of the reagent and gastric juice and evaporate in a porcelain dish. A red residue remains if free hydrochloric acid is present. The reaction is sensitive to 1:10,000.

Reactions of Phloroglucinol. Wenger and co-workers¹⁰ have studied the reactions of phloroglucinol with various ions, and have found a number of them are sufficiently distinctive to serve as satisfactory tests. These reactions are shown in Table 28.

TABLE 28.—REACTIONS OF PHLOROGLUCINOL

Ion	Reaction
Ceric	Brown precipitate in an acid solution.
Stannous	In an alkaline medium, stannous tin gives a rose color which changes to yellow. A precipitate forms in a more concentrated solution.
Arsenite	A fuchsin red color in an alkaline medium. Pentavalent arsenic gives no color.
Antimonous	A red color in an alkaline medium.
Antimonic	A yellow color is obtained if the reagents are mixed in the following order: antimony + phloroglucinol + sodium hydroxide.
Chromous	A red color in an alkaline medium.
Ferric	A blue-violet color in an acid solution.
Palladous	A greenish color.
Osmium (Os ⁶⁺)	A violet-black color in an alkaline medium.
Vanadium	
(VO ₃ ⁻ and VO ₄ ⁻³)	A feeble yellow color in an alkaline medium.
Nitrite	A yellow color in an alkaline medium.
Bromate	A yellow-brown precipitate in an acid medium.
Dichromate	A black color.

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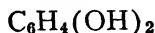
PYROCATECHOL

Synonym: Pyrocatechin, catechol, o-dihydroxybenzene, pyrocatechuic acid



Mol. Wt. 110.11

Beil. Ref. VI, 759.



Use: Detection of aluminum, cerium, cobalt, columbium, iron, molybdenum, nitrite, oxygen, titanium, tungsten and vanadium.

Determination of gold, iron, oxygen and vanadium.

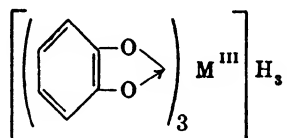
Pyrocatechol is a white crystalline solid which becomes discolored upon exposure to air and light. It melts at 103-104° C. and boils at 240-245° C. It sublimes,

and is volatile with steam. The compound dissolves in 2.3 parts of water, and is soluble in alcohol, benzene, chloroform and ether.

Preparation: Dissolve 12.2 g. of pure salicylaldehyde in 100 ml. of N sodium hydroxide solution at room temperature and add 142 g. of 3 per cent hydrogen peroxide. Allow the mixture to stand for 15-20 hours and add a few drops of acetic acid to neutralize any excess alkali, and finally evaporate the solution to complete dryness on a water bath under reduced pressure.

Grind the solid to a fine powder and warm almost to boiling with 50 ml. of toluene and then pour into a fluted filter paper which is placed in a large funnel, the stem of which passes through a cork into a flask containing toluene. Extract the product by heating the flask containing the toluene, while a second, round-bottom flask is placed on the funnel and held in place by clamping to a ring stand. Cold water is run through the upper flask, which acts as a condenser. Continue the extraction for 5 hours. Allow the toluene to cool and pour off from the pyrocatechol which separates as a crystalline solid. Again grind the insoluble material and repeat the extraction with the toluene previously used. Purify by distilling the crude product under reduced pressure (B.P. = 119-121°/10 mm.) and recrystallize the distillate from about 5 times its weight of toluene.¹

Pyrocatechol, like other polyhydroxy compounds, forms inner-complex compounds in which the hydrogen atom of one hydroxyl group is replaced by one equivalent of a metal, which in turn is coordinated to the oxygen atom of the second hydroxyl group. This gives rise to compounds of the type



In alkaline solutions salts of these acids are formed. Many of the analytical uses of pyrocatechol are based on this property.

Detection of titanium. Pyrocatechol reacts with neutral and dilute aqueous solutions of titanium salts to form a yellowish-red colored compound. According to Rosenheim and co-workers² this reaction depends upon the formation of an inner complex pyrocatechate of tetravalent titanium, $\text{H}_2[\text{C}_6\text{H}_4\text{O}_2\text{Ti}-(\text{O}_2\text{C}_6\text{H}_4)_2]$.

This reaction was observed by Piccard^{3,4} and others,^{5,6} who suggested its use for the detection of small quantities of titanium. The reaction can be carried out as a spot test by means of the following procedure:

Procedure: Acidify the solution to be tested with sulfuric acid and place a drop of this solution upon a strip of filter paper which has been impregnated with a freshly prepared 10 per cent aqueous solution of pyrocatechol. A more or less deep yellow-red spot appears according to the amount of titanium present. By means of this reaction 2.7γ of titanium can be detected at a dilution of 1:19,000.

Large quantities of free mineral acids interfere, and alkali carbonates and hydroxides reduce the sensitivity. Salts of trivalent iron should not be present since they also yield a colored compound with pyrocatechol. Colored ions of the ammonium sulfide group also interfere. This test is most satisfactorily employed after previous separation of titanium from interfering substances.

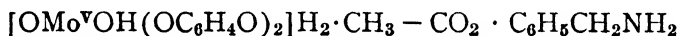
Pike⁷ and co-workers have studied the titanium-pyrocatechol reaction for possible interference by other ions. As a reagent they used a 10 per cent aqueous solution of pyrocatechol containing 1 drop of 6 N sulfuric acid per 100 ml. The test was carried out by mixing 1 ml. of this reagent with 10 ml. portions of the solution to be examined. They found a positive test was obtained with titanium solutions having a concentration of 0.00001 mole per liter. No interference was caused by aluminum, ammonium, barium, beryllium, cadmium, cerium, cesium, cobalt, lanthanum, lead, manganese, molybdenum, potassium, rubidium, sodium, strontium, tellurium, tungsten, zinc, chloride, molybdate, nitrate, nitrite, sulfate and sulfite. On the other hand, antimony, arsenic, bismuth, chromium, copper, iron, lithium, magnesium, mercury, nickel, silver, tin, thallium, thorium, uranium, vanadium, acetate, chromate, phosphate, phosphite, vanadate and selenium caused interference.

According to Kuznetsov,⁸ trivalent titanium does not give the pyrocatechol reaction, and consequently this reagent serves to differentiate between the two oxidation states of the metal.

Detection of molybdenum, vanadium, tungsten and columbium. Martini⁹ used pyrocatechol and benzylamine in a microchemical test for molybdenum, vanadium and tungsten.

Procedure. To 1 drop of 1 per cent ammonium molybdate solution add small quantities of pyrocatechol until the liquid is orange-red in color; and then add, from a small stirring rod, a very small drop of benzylamine. Next add a little 14 per cent acetic acid and stir quickly with a glass rod. Round orange-colored groups of crystals appear.

Similar tests are obtained with vanadium and tungsten, although the color of the vanadium compound is light yellow and that of the tungsten compound black. Martini assigns to the molybdenum compound the following formula:



Tartarini¹⁰ claims, however, that the reaction product of pyrocatechol and molybdic and tungstic acids have hexavalent molybdenum and tungsten atoms rather than the pentavalent atoms as indicated by Martini. A similar test is obtained by using pure aniline or piperazine instead of benzylamine. Characteristically colored crystalline precipitates are obtained with molybdenum, tungsten and vanadium when a saturated solution of pyrocatechol acetate and the organic bases are added.^{11,12,13} With aniline and pyrocatechol acetate, ammonium molybdate yields orange-colored crystals, sodium tungstate yields yellow crystals, and soluble vanadium salts yield black precipitates.

A 1:10,000 solution of ammonium vanadate reacts with pyrocatechol to give a blue color which can be used for the detection of as little as 0.4γ of vanadium.¹⁴

Szebelledy and Ajtai ¹⁵ have used pyrocatechol in a sensitive test for vanadium. This test is based upon the fact that vanadium catalyzes the reaction between p-phenetidine and potassium bromate, and the presence of pyrocatechol increases this catalytic effect.

Procedure. Add 1 ml. of a 1 per cent solution of pyrocatechol to the solution to be tested, and add 1 ml. of 0.1 per cent p-phenetidine, 1 ml. of saturated potassium bromate solution and sufficient water to make 5 ml. of solution. Prepare a blank using the same reagents, but in which distilled water is substituted for the vanadium solution. In a few minutes the solution containing vanadium becomes violet colored, whereas the blank solution remains colorless. As little as 0.001 γ of vanadium can be detected by this method.

The above test can be carried out in the presence of most common ions.

The above reaction has been made the basis for a quantitative procedure for vanadium by Szebelledy and Ajtai ¹⁶:

Procedure. Place 1 ml. of the solution to be analyzed in a carefully cleaned test tube and add 1 ml. of 0.1 per cent p-phenetidine, 1 ml. of 1 per cent, freshly prepared pyrocatechol and sufficient water to make 4 ml. of solution. Shake the mixture and quickly blow into it from a micropipet 1 ml. of 5 per cent potassium bromate solution. Start a stop watch immediately. Transfer 1 ml. of the reaction mixture to the optical vessel of a photometer and note the time when the galvanometer reaches the scale marked 50. From this time the quantity of vanadium present can be calculated by comparing with values obtained using solutions of known vanadium content.

Another procedure consists in measuring the time taken for the needle to reach the divisions, 90, 80, 70, etc.

By means of the foregoing methods as little as 0.0006 γ of vanadium can be determined.

A yellow color appears when pyrocatechol and a concentrated solution of sodium acetate are mixed with a solution containing columbium. As little as 0.4 γ of columbium can be detected by this reaction. Molybdenum, tungsten, iron, titanium and mineral acids interfere.^{17,18}

Detection of iron and aluminum. When a moderately concentrated solution of pyrocatechol in acetic acid is added to a solution containing ferric ions, an amorphous violet precipitate is formed. The addition of aniline causes the formation of cubic crystals, and finally violet platelets. This test may be used for the detection of less than 0.2 γ of iron.

Under similar conditions 1 γ or more of aluminum yields star-shaped clusters of lenticular crystals. Chromium does not give a similar reaction.¹⁹

Determination of iron. Pyrocatechol reacts with ferric iron in a faintly acid solution to give a dark green color. If the solution is faintly alkaline, or if the concentration of iron is less than 0.01 N the color is a brilliant violet. The compound produced in an alkaline solution is the salt of the acid $[(C_6H_4O_2)*Fe]H_8$. The violet color is suitable for a colorimetric comparison.²⁰

Procedure. Add 10 ml. of a 1 per cent aqueous solution of pyrocatechol to 50 ml. of the solution containing ferric iron. Shake and dilute to 100 ml., and compare with a freshly prepared 0.002 N solution of ferric chloride. This is prepared by dissolving 0.1081 g. of ferric chloride in sufficient water to make 1 liter of solution. A 50 ml. sample of this solution when treated with the reagent and diluted to 100 ml. becomes 0.001 N, and corresponds to 0.0186 mg. of iron per ml.

Detection of cobalt. A red precipitate is formed when ammonia is added to an aqueous solution containing pyrocatechol and a cobalt salt.^{21,22} The following compounds are obtained when ammonia is used as the precipitant, $[(C_6H_4O_2)_2Co]H_2 \cdot 5\frac{1}{2}H_2O$ and $[(C_6H_4O_2)_2Co](NH_4)_2$.

Detection of cerium. A violet precipitate of $[Ce(C_6H_4O)_3](OH)_3$ is formed when a solution of a ceric salt is treated with pyrocatechol and ammonium hydroxide. This compound darkens in air and is completely soluble in acids and strong bases. In the presence of an excess of ammonium hydroxide, the violet salt $[Ce(C_6H_4O)_3](ONH_4)_3$ is formed. This reaction may be used for the detection of small quantities of cerium. One part of cerium per million parts of solution can be detected in the absence of the rare earths, which also give colored compounds with pyrocatechol. One part of cerium in 400,000 parts of water is easily detectable.

Since alkaline solutions of pyrocatechol turn brown in air, the violet color produced by the reaction with ceric salts may be obscured. The addition of sodium thiosulfate, however, delays the formation of the brown color and is useful in the detection of cerium.²³

Determination of gold. Beamish and co-workers²⁴ have found that gold is quantitatively precipitated by reduction with pyrocatechol; hence, pyrocatechol may be used to replace hydroquinone in the determination of gold by reduction to the metallic state.

Detection of nitrites. Vagi²⁵ has used pyrocatechol and sulfanilic acid for the detection of nitrites. A sensitive reagent is prepared by dissolving 1 g. of pyrocatechol and 0.5 g. of sulfanilic acid in 100 ml. of acetic acid and diluting with 300 ml. of water. A pink color is obtained with 5 ml. of water containing 0.1-1.0 mg. of N_2O_3 per liter. Nitrates give no similar color.

Both nitrates and nitrites, however, yield a green coloration with a 1 per cent solution of pyrocatechol in concentrated sulfuric acid.²² Castiglioni^{26,27} has also used pyrocatechol in a color reaction for nitrites. This test is carried out by adding several mg. of pyrocatechol to 1 ml. of solution, heating the mixture to boiling, and making alkaline with sodium hydroxide. A wine-red color is obtained with sodium nitrite at a dilution of 1:1,000,000.

Detection and determination of oxygen. A deep red color is obtained when a solution of a ferric salt and pyrocatechol is made alkaline with sodium or potassium hydroxide. This color is due to the formation of a salt of the acid, $[Fe(C_6H_4O_2)_3]H_3$. A colorless solution is obtained, however, when a solution of a ferrous salt and pyrocatechol is made alkaline with sodium or

potassium hydroxide, but this turns red with the addition of very small quantities of oxygen. According to Binder and Weinland^{28,29} this reaction constitutes a delicate test for oxygen.

Reagent. Dissolve 14 g. of ferrous sulfate and 18 g. of pyrocatechol in 75 ml. of water, acidify with 10 drops of sulfuric acid, and add a cooled solution of 33 g. of potassium hydroxide in 75 ml. of water.

Procedure. The above reagent turns red upon exposure to a gas containing free oxygen.

Novonty and Toul³⁰ have studied this test and report that it is possible to obtain a faint test even when no oxygen is present.

Binder and Weinland³¹ state that the reagent described above is satisfactory for the quantitative absorption of oxygen in gas analysis.

Determination of borates. Mellon and Morris³² have studied the use of polyphenols as possible substitutes for compounds, such as glycerol and mannitol in the titration of boric acid, but they report these reagents are unsatisfactory.

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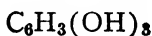
PYROGALLOL

Synonym: Pyrogallic acid, 1,2,3-trihydroxybenzene



Mol. Wt. 126.11

Beil. Ref. VI, 1071.



Use: Detection of antimony, barium, bismuth, calcium, cerium, cobalt, columbium, copper, gold, iodate, iron, lanthanum, molybdenum, neodymium, nitrate, nitrite, osmium, praseodymium, strontium, tantalum, thorium, titanium and vanadium.

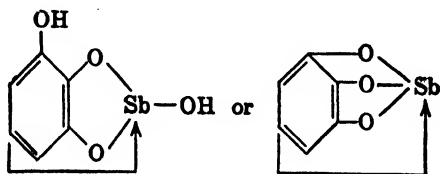
Determination of aluminum, antimony, bismuth, boric acid, cadmium, carbon monoxide, cerium, columbium, gold, iodate, iron, molybdenum, nitrate, nitrite, oxygen, silver, tantalum and titanium.

Pyrogallol consists of white odorless crystals which become gray on exposure to air and light. It melts at 131-133° C. and boils at 309° C. One gram of the solid dissolves in 1.7 ml. of water, 1.3 ml. of alcohol and 1.6 ml. of ether. It is slightly soluble in benzene, chloroform and carbon disulfide.

Pyrogallol reacts with oxygen to form a brown oxidation product. For this reason it is necessary to prepare reagent solutions only a short time before use, and to use boiled, air-free distilled water for this purpose.

Pyrogallol to be used for quantitative determinations must be tested for purity. In addition to determining the melting point (131° C.), the material should be checked for inorganic contaminants. This is accomplished by igniting 1 g. of pyrogallol in a weighed platinum or quartz crucible: the pyrogallol should sublime without weighable residue. To test for tannic acid, dissolve 2 g. of pyrogallol in 5 ml. of ether. A clear solution is obtained if tannic acid is absent.

Detection and determination of antimony. Pyrogallol forms with antimony and bismuth complex salts which may be used for the detection and determination of these metals. The benzene ring appears to be necessary for the formation of these complexes, since glycerol, in which three hydroxyl groups are attached to an aliphatic nucleus, does not give similar reactions with bismuth and antimony salts. For this reason Feigl³ assigns to the antimony compound the following formula:



in which the dependency of the benzene ring is shown by the coordination bond. This structure is supported by several facts: the formation of a 5-membered

ring is probable since similar structures are known to be favorable to the formation of stable inner-complexes. The four coordination value for antimony is supported by the existence of the halogen double salt of antimony trichloride. Further, antimony is known to add to aromatic hydrocarbons to form colored addition products.¹¹²

The formation of a white crystalline precipitate when pyrogallol is added to dilute acid solutions containing trivalent antimony has been used by Feigl^{11,12} as a sensitive test for antimony.¹⁰⁸ The reaction is best carried out with a dilute hydrochloric acid solution containing tartaric acid or a tartrate. A distinct test is obtained with as little as 4.6 mg. of antimony per liter of solution.

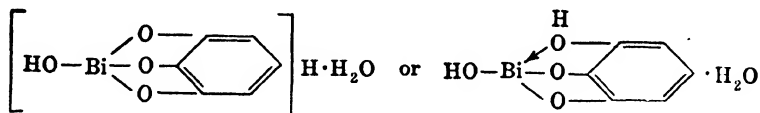
Since the precipitation of antimony with pyrogallol is quantitative, this reagent may be used for the determination of antimony.

Procedure. To a solution containing trivalent antimony, add sufficient sodium potassium tartrate to prevent precipitation of the basic salt on dilution, and then add about 5 times the theoretical quantity of pure pyrogallol dissolved in 100 ml. of distilled water. Add the reagent all at one time and dilute the mixture to 250 ml. with water. Allow to stand 2 hours, filter through a filter crucible, and wash 3 times with 50-ml. portions of cold water. Dry the precipitate at 100-105° C. and weigh. Again wash several times with water, dry and check for constant weight. The factor is 0.4601.

This procedure can be used for the separation of antimony and arsenic, since the latter is not precipitated with pyrogallol.

Detection and determination of bismuth. Like antimony, bismuth is quantitatively precipitated as a yellow crystalline compound when a solution of bismuth salt which has an acidity not greater than 0.1 N is treated with pyrogallol. This reaction may be used for the detection and determination of bismuth.^{1,2,108}

Feigl³ has assigned to the bismuth compound the same structure as that of the antimony salt. The following formulas have been proposed by Takagi and Nagase.⁴



Pyrogallol reacts with bismuth salts in a nitric acid solution to form an orange-yellow precipitate which is used for the detection of small quantities of bismuth.^{1,5} Feigl⁵ has found that by shaking the mixture with ether a yellow zone is formed, which increases the sensitivity of the test. By means of this reaction 71γ of bismuth per ml. of solution can be detected.

The following method proposed by Feigl and Ordelt¹¹ may be used for the determination of bismuth:

Procedure. To an acid solution of a bismuth salt add 0.5 N ammonium hydroxide until a permanent turbidity of the basic salt is formed. The solution should not be more than 0.02 N in ammonia. Then add dropwise a 0.1 N solu-

tion of nitric acid until the turbidity just disappears, and add a concentrated solution of pyrogallol until precipitation is complete. Filter, wash with 0.1 N nitric acid and then with pure water. Dry at 110° C., and weigh. The factor for bismuth is 0.6295.

This method may be used for the separation of bismuth from lead, copper, cadmium, and zinc. Ostroumov ^{7,110} has studied various methods for determining bismuth in the presence of lead and copper, and reports that best results are obtained by three methods: that of Moser and Maxymowicz,⁹⁸ using potassium bromide and potassium bromate; by use of pyrogallol; and with cupferron. Strebinger and Flaschner ⁸ have used the method of Feigl and Ordelt ⁶ for the microdetermination of bismuth:

Procedure. Treat the nitric acid solution of bismuth nitrate with ammonium hydroxide until a faint opalescence appears, and add a little solid pyrogallol. Heat the mixture on a water bath for 15 minutes and collect the precipitate in a filter tube. Wash the precipitate alternately with water and benzene to prevent creeping, then dry at 110° C. and weigh.

Teitelbaum ⁹ has used pyrogallol in a colorimetric method for the determination of bismuth. Bismuth is precipitated with pyrogallol, and the precipitate is then dissolved in hydrochloric acid and treated with Folin's reagent.¹⁰ The resulting color is compared colorimetrically with that of solutions of known bismuth content.

Reagent. *Folin-Denis reagent:* Mix 4 g. of phosphomolybdic acid and 20 g. of sodium tungstate with 10 ml. of 85 per cent phosphoric acid and 150 ml. of water and boil for 2 hours under reflux. Cool, and dilute to 200 ml. Filter if necessary.

Procedure. Place the material to be analyzed in a centrifuge tube and mix with 3-4 mg. of solid pyrogallol or 2-3 drops of freshly prepared 4 per cent pyrogallol solution. Warm to 70° C. and add 0.33 N ammonium hydroxide to the appearance of a turbidity. Heat just to boiling and add 1-2 drops of a 0.1 per cent solution of thymol blue in 20 per cent alcohol, and add ammonium hydroxide until the solution is alkaline to the indicator. Suspend this solution in the centrifuge tube in a boiling water bath for 10 minutes and allow to cool. Dilute to 5 ml. and centrifuge for 10 minutes at 2000-2500 r.p.m. Decant the clear liquid, add 5 ml. of water and stir the solid with a glass rod. Again centrifuge and finally repeat the washing several times using 2 ml. of water. Dissolve the precipitate in 1 ml. of 4 N hydrochloric acid and wash with 15-20 ml. of water into a small flask. Next add 0.5-1.0 ml. of Folin's reagent and 6 ml. of a saturated solution of sodium carbonate. Dilute the mixture to 30 ml., allow to stand for about 25 minutes and compare the resulting blue color with that of standards similarly prepared.

Detection and determination of molybdenum. An orange color is obtained when pyrogallol is added to a solution containing molybdenum and acetic

acid. Moir¹³ claims that this reaction constitutes a more sensitive test for molybdenum than a similar procedure employing tannin.

Martini¹⁴ has used pyrogallol for the microchemical detection of molybdenum. The reaction depends on the formation of an orange pyrogallol-acetic acid-piperazine complex, which possesses a triclinic crystalline structure.

Procedure. Add pyrogallol to a drop of ammonium molybdate solution and add a drop of acetic acid and a drop of a concentrated solution of piperazine. Molybdenum is detected by means of the characteristic orange crystals.

Alekseev¹⁵ has substituted pyrogallol for tannin in a procedure for the colorimetric determination of molybdenum. The intensity of the color obtained in the presence of an excess of pyrogallol is a function of the molybdenum concentration and the pH of the solution. The same color range of equal intensities, from colorless through yellow and orange to orange-red is produced at a definite pH by increasing the molybdenum concentration, and at a definite molybdenum concentration by increasing the pH of the solution. The rate of spontaneous oxidation and discoloration of pyrogallol solutions increases rapidly at higher pH values. At the optimum pH of 4.4 the color reaction is stable for 1 hour, and can be successfully used for the determination of molybdenum. The reagent is prepared by dissolving 10 g. of pyrogallol and 20 ml. of glacial acetic acid in sufficient water to make 1 liter of solution. Best results are obtained with 0.05-1.0 mg. of molybdenum in 10 ml. of solution, although the reaction is sensitive to a minimum of 0.001 mg. of molybdenum at a concentration of 1:10,000,000. Pozzi-Escot¹⁰¹ claims that the intensity of the color produced in the reaction between pyrogallol and molybdic acid is not proportional to the molybdenum content.

Iron and tungsten also give color reactions with pyrogallol, and consequently must be absent while making the determination. They are best removed by the method of Ugniyachev¹⁶ and Spurge.¹⁷

Detection and determination of gold. A red or violet color is obtained when gold chloride is reduced with stannous chloride. This reaction is due to the precipitation of finely divided gold on stannic hydroxide. Donau¹⁸ applied this reaction to the detection of gold by impregnating silk fibers with stannous chloride and pyrogallol. This reaction has been studied further by Cole,¹⁹ who recommends the following procedure:

Reagent. Dissolve 10 g. of stannous chloride in 95 ml. of distilled water and 5 ml. of concentrated hydrochloric acid. Filter and to the filtrate add 10 g. of pyrogallol. Place viscose silk fibers in this solution, and heat for 10 minutes on a water bath. Remove the fibers, wash well with water, and dry between strips of filter paper. The reagent is stable for 6 months.

Procedure. Place a drop of the solution to be tested on a glass slide and insert a piece of the prepared fiber about 5 mm. long for about half of its length. Allow the drop to evaporate to dryness. A red or purple color appears if gold

was present in the test solution. Old fibers are turned blue by concentrated gold solutions. The test is sensitive to 0.05 g. of gold per liter.

Alkali hydroxides prevent the formation of the color, and mineral acids retard its development. Oxidizing and reducing agents also interfere. Silver nitrate turns the fiber yellow to brown in the absence of gold, but unless present in excessive amounts it does not obscure the color due to gold. Ammonium molybdate and ammonium phosphomolybdate cause the fibers to turn light blue.

Korenman²⁰ has used the method of Donau^{18,21} for the microchemical detection of gold. As a reagent he used photopaper impregnated with a dilute solution of stannous chloride and pyrogallol. This paper turns grayish-blue or blue in the presence of gold. This test will detect as little as 0.016 γ of gold at a dilution of 1:15,600.

Costeanu^{22,23} has used the foregoing method for the semi-quantitative determination of gold. By comparing spots produced on paper impregnated with the reagent with those obtained by using solutions of known gold content the approximate concentration of the unknown can be determined.

Saul¹⁰⁴ performs the test by adding 1 ml. of a 0.1 per cent solution of pyrogallol to 10 ml. of the gold chloride solution. A violet color is obtained with 0.002 per cent gold chloride.

Beamish and co-workers²⁴ have also used pyrogallol in place of hydroquinone for the quantitative precipitation of gold.

Detection and determination of columbium and tantalum. Columbium reacts with pyrogallol in the presence of sodium sulfite in an alkaline solution to produce a stable yellow color. No color is obtained with columbium when treated in an acid solution. Tantalum, on the other hand, yields the same color as columbium, but only in an acid solution. In a solution containing both columbium and tantalum, columbium is determined by adding sodium sulfite to the alkaline sulfite solution and then treating with pyrogallol and comparing with a standard. Tantalum is determined after acidifying with sulfuric acid.^{25,26,27,114}

The oxides of columbium and tantalum, and titanium, which are usually present, are fused with sodium bisulfate, and the solution of the melt is then treated with ammonium oxalate solution. To determine columbium the solution is mixed with an equal amount of a 5 per cent solution of pyrogallol in a saturated aqueous solution of sodium sulfite and the intensity of the resulting color determined. Tantalum in an alkaline solution does not interfere with this determination but titanium gives a color similar to that produced by columbium. A correction can be made for small quantities of titanium, which is determined by the hydrogen peroxide method. If present in quantities greater than that of the columbium, titanium must be removed.

Tantalum is determined colorimetrically with pyrogallol in an acid solution without the use of sodium sulfite. Columbium and titanium do not interfere.²⁸ Thanheiser²⁹ has used the yellow coloration produced by tantalum with pyrogallol in a 3 per cent ammonium oxalate solution for the photometric determination of tantalum in steel. Since titanium also gives a yellow color with pyrogallol, it must be determined independently and correction applied.

A solution prepared by dissolving 5 g. of ammonium chromate in 250 ml. of water can be used as a color standard in the tantalum and columbium determination.²⁷

Columbium and tantalum may be detected by means of yellow color produced in the above reaction. By means of pyrogallol 0.05 mg. of Cb_2O_5 and 0.05-0.07 mg. of Ta_2O_5 in 1 ml. of solution can be detected.

Alimarin and Frid^{30,31,113} have used pyrogallol for the separation of columbium and tantalum from iron, zirconium and titanium in the analysis of minerals, rocks and metals. Columbium and tantalum are precipitated by benzenearsonic acid in a tartaric acid solution in the absence of zinc, zirconium and titanium. These latter metals are removed with the aid of pyrogallol in the following manner:

Procedure. Grind the mineral to a fine powder and fuse with potassium pyrosulfate. Treat the melt with a 5 per cent solution of pyrogallol. Iron, zirconium and titanium form pyrogallates and pass into solution. Most of the columbium (brown precipitate) and tantalum (yellow precipitate) remain undissolved. Treat the pyrogallol solution with an excess of ammonium hydroxide until the solution has a strong odor of ammonia and then warm. With this treatment columbium and tantalum dissolve and the solution becomes clear and yellow. Neutralize the solution with hydrochloric acid and add an excess, which is so measured that the acid content of the solution is about 1 N. Heat the solution to boiling and filter off the brown precipitate of tantalum and columbium. Wash with a 1 per cent acidified solution of the reagent and ignite in a porcelain crucible.

Titanium may also precipitate if present in large quantities, and in this case the separation should be repeated. One separation is sufficient to remove iron and zirconium completely.

Detection of titanium. A deep reddish-brown solution is obtained when 3 moles of pyrogallol are added to an ether solution containing 1 mole of titanium chloride. By removing the ether and adding concentrated ammonium hydroxide a dark reddish-brown crystalline compound of $\text{HOTi}[\text{OC}_6\text{H}_5(\text{OH})\text{ONH}_4]_3 \cdot 3\text{H}_2\text{O}$ is obtained.^{32,107,108}

Titanium in an alkaline or acid ammonium oxalate solution reacts with pyrogallol to give a yellow color.²⁵

Detection and determination of cerium, thorium and the rare earths. Solutions of cerium, thorium, lanthanum and trivalent titanium yield colored precipitates when treated with a little ammonium hydroxide and 10 ml. of a 1 per cent solution of pyrogallol. This reaction is especially useful as a delicate test for cerium, which yields a violet or dark-blue precipitate, depending upon the concentration of the reagents. With a high concentration of ammonium hydroxide and a low concentration of pyrogallol, a violet colored sol is obtained which may be used for the colorimetric determination of cerium.³³

Iron, aluminum, chromium, manganese, nickel, cobalt and uranium do not give similar reactions. Ethylenediamine can be substituted for ammonium hydroxide in this reaction.³⁴

Pyrogallol reacts with ammoniacal solutions of praseodymium and neodymium salts to yield white precipitates.³⁵ Wenger and Duckert³⁶ have investigated the use of pyrogallol as a reagent for thorium but report that it is unsatisfactory, since the reaction is too general and gives similar reactions with accompanying elements, such as the rare earths and uranium.

Detection of copper. Copper may be detected by adding a little pyrogallol to a concentrated solution of sodium sulfite and adding a solution of copper salt. A reddish-yellow to red color is produced with as little as one part of copper in three million parts of solution.^{37,38,111}

Determination of silver. Costeanu³⁹ has used a spot test employing pyrogallol for the estimation of small quantities of silver.

Procedure. Strips of filter paper are impregnated with a saturated solution of pyrogallol and dried in air. A series of drops of silver nitrate solutions of known but different concentrations are then placed on each strip to form a series of differently colored spots. These serve as a comparison series when arranged in the order of increasing intensity.

The solution to be analyzed is diluted to a definite volume and a drop of this is placed on a strip of paper prepared as above. The color of the resulting spot is compared with the standard series.

Detection of vanadium. Pyrogallol reacts with a solution of vanadic acid to give a blue color which may be used for the detection of vanadium. This reaction is sensitive to 0.1 mg. of V_2O_5 per liter of solution. By using 0.5 ml. of solution, 0.00005 mg. of V_2O_5 can be detected.⁴⁰

Martini¹⁴ has used pyrogallol in a microchemical test for vanadium which is based upon the formation of a black microtriclinic pyrogallol-o-toluidine complex.

Detection and determination of iron. Iron salts react with pyrogallol to give a violet coloration. This reaction may be used for the detection and colorimetric determination of iron. In a procedure used by Agostini,¹⁰⁵ the iron solution is treated with nitric acid, and iron precipitated with sodium hydroxide. The precipitate is dissolved in hydrochloric and nitric acid and the mixture treated with pyrogallol. Ferric salts give an intense red color.

Pyrogallol reacts with iron salts in the presence of sodium sulfite to yield a violet color. This reaction has been used by Palkin⁴¹ for the colorimetric estimation of small quantities of iron.

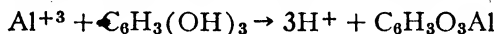
Reagents. *Pyrogallol reagent:* Dissolve 5 g. of pyrogallol in 100 ml. of a saturated sodium sulfite solution.

Standard solution: A standard solution containing 0.0025 g. of iron per ml. is prepared by dissolving 0.1244 g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water and diluting to 1 liter.

Procedure. To a solution of iron salt, add sulfuric acid until slightly acid. Dilute with water until a sample when withdrawn and treated with the pyrogallol reagent gives approximately the same color intensity as the standard solution when similarly treated. To a 5 ml. aliquot of the unknown solution, add 85 ml. of water, and then add the reagent dropwise to a constant color and compare with the standard solution. This method is sensitive to 1% of iron.

Salts containing colored ions such as copper, nickel, cobalt and chromium must be removed before making the determination.

Determination of aluminum. Aluminum salts react with an aqueous solution of pyrogallol according to the following equation



to form aluminum pyrogallate and free hydrogen ions. The hydrogen ion can be titrated with 0.1 sodium hydroxide, using methyl red as an indicator, and the aluminum equivalent can be determined by use of the above equation.⁴²

Determination of cadmium. Pyrogallol is used as an indicator in the titration of cadmium by means of a solution of ammonium molybdate. The volume of the precipitant necessary for complete reaction with cadmium is determined by using a saturated solution of pyrogallol in chloroform as the indicator.⁴³

Detection of calcium, strontium and barium. Pyrogallol gives color reactions with calcium, strontium and barium, but these do not appear to be important analytically.¹⁰⁹

Reactions with metals. Wenger and co-workers¹⁰² have studied the reactions of pyrogallol with various cations, and report a number of useful analytical reactions in Table 29.

TABLE 29.—REACTIONS OF PYROGALLOL

Ion	Reaction
Fe^{+3} and Fe^{+2}	Violet coloration ✓
Os^{+4} and Os^{+8}	Blue green to violet color
V^{+3}	Intense blue black color
Bi^{+3}	Yellow precipitate
Ti^{+3} and Ti^{+4}	Red-brown color in alkaline medium
Cu^+ , Cu^{+2} , Ag^+ , Au^{+3} , Hg^+ , Hg^{+2}	Reduced to metal ✓

Detection and determination of nitrites and nitrates. An aqueous solution of pyrogallol acidified with sulfuric acid is colored brown by the addition of nitrite. This reaction has been used by Schoenbein⁴⁶ and others⁴⁷⁻⁴⁹ as a

sensitive test for nitrite. By means of this reaction it is possible to detect 1 part of nitrite in 50,000 parts of water.

Rosenfeld ⁴⁴ performs this test as follows:

Reagent. Dissolve 0.5 g. of pyrogallol in 90 ml. of water and 10 ml. of concentrated sulfuric acid.

Procedure. Mix 2 ml. of the reagent with 100 ml. of water to be tested. A yellow color forms immediately with as little as 0.4 mg. of N_2O_3 per liter. By allowing the mixture to stand for about 25 minutes, 0.2 mg. of N_2O_3 per liter can be detected.

Vagi ⁴⁵ recommends the following procedure:

Procedure. Add 5 ml. of a 1 per cent solution of pyrogallol in 50 per cent acetic acid to 40 ml. of aqueous solution to be tested. With nitrite a reddish-brown coloration is obtained, and this becomes yellowish on standing.

Nitrate gives no color with this reagent. Pyrogallol reacts with nitrate in the presence of sulfuric acid, however, to give color reactions which may be used for the identification of nitrates. Curtman ⁴⁷ has stated that a solution of pyrogallol in sulfuric acid is colored yellow by nitric acid. The sensitiveness of this reaction is 1:500,000. Horsley, ⁴⁸ using a solution of pyrogallol in concentrated sulfuric acid, has obtained a violet-blue color with nitrate. Vagi ⁴⁵ states that both nitrites and nitrates give a green coloration with a 1 per cent solution of pyrogallol in concentrated sulfuric acid.

Rosenfeld ⁴⁴ performs the nitrate test as follows:

Reagent. Dissolve 0.5-1.0 g. of pyrogallol in 100 ml. of water.

Procedure. Mix 3 ml. of the solution to be tested with 6 ml. of concentrated sulfuric acid and add 1 drop of reagent. In the presence of nitrate, the upper layer becomes violet to dark-brown within a few minutes.

The color reaction of pyrogallol with nitrate may be used for the colorimetric determination of the latter. The following procedure is used by de Nardo ⁵⁰ for the determination of nitrates in soil and in water. This method is used if the concentration of nitrate exceeds 0.01 mg. of potassium nitrate, but for lower concentrations pyrogallolsulfonic acid should be used (page 00). A rose to brownish-red, olive-green or black color is obtained depending upon the concentration of nitrate.

Reagent. Dissolve 5 g. of pyrogallol in water, add 0.2 g. of sodium bisulfite and dilute to 200 ml.

Procedure. Mix 100 g. of soil with 200 ml. of distilled water and shake for 1 hour. Filter and collect 80 ml. of the filtrate, and to this add 3 ml. of saturated barium hydroxide solution. Heat to boiling and allow to stand, and then add 1 ml. of 50 per cent basic lead acetate solution. Let stand for 2 or 3 minutes and add 5 ml. of saturated sodium sulfate solution. Cool, dilute to

100 ml., and shake well. Filter and collect 10 ml. of the filtrate. This corresponds to 4 g. of the sample.

If the quantity of nitrite exceeds 0.01 mg. of N_2O_3 in the 100 g. sample of soil used, add 1 drop of a saturated urea solution and 1 ml. of concentrated sulfuric acid. Nitrites are completely destroyed within 10 minutes.

To 5 ml. of the filtrate obtained above, add 5 ml. of pyrogallol reagent and mix well. Add 25 ml. of concentrated sulfuric acid and again mix. Allow to stand for 1 hour and compare with a series of standards similarly and simultaneously prepared.

Various ions interfere by giving color reactions with pyrogallol. Ferric iron yields a violet-red color, iodates a violet color, chromates a yellow color and organic matter a brown color. Nitrite gives the same color reaction as nitrate. Small quantities of chlorate, ferrous ion, chloride and bromide do not interfere.

To determine nitrate in water by the above method, use a 100 ml. sample, but omit the addition of barium hydroxide and basic lead acetate unless considerable quantities of ferric iron, iodide or organic matter are present.

Pyrogallol has been recommended for a quick and approximate estimation of nitrates in sewage affluent and water.^{51,52}

Procedure. To 10 ml. of sample in a test tube, add about 0.2 g. of pyrogallol and mix thoroughly. Add 2 ml. of concentrated sulfuric acid in such manner that it flows down the side of the tube and forms a layer at the bottom. Deliver the sulfuric acid from a pipet, placing the tip of the pipet just below the surface of the liquid. Now add 0.1 g. of powdered sodium chloride, which causes an effervescence at the junction of the two liquids and the formation of a purple ring. The amount of nitrate is proportional to the intensity and size of the purple ring. The determination is made by comparing the ring produced in the unknown with that in a standard solution prepared by dissolving 0.1872 g. of potassium nitrate in sufficient water to make a liter of solution. One ml. of this solution contains 0.1 mg. of N_2O_5 .

Pyrogallol is used in the preparation of pyrogallolsulfonic acid, which is a sensitive reagent for nitrate and nitrite (page 262).

Detection of iodate. Pyrogallol is oxidized by iodates in an acid solution to form purpurgallin, which imparts a brick-red to dark-brown coloration to the reaction mixture. This reaction has been used by Gotlib⁵³ for the detection and determination of small quantities of iodate.

For a spot test, use a strip of filter paper that has been saturated with oxalic acid, and then with a 6 per cent solution of pyrogallol in acetone. The sensitivity of this reaction is 1:200,000. Ferric iron, nitrate, chlorate, perchlorate and silicofluoride do not interfere. Iodide, chromate and dichromate interfere and persulfate and bromate produce different colors.

The following procedure may be used for the colorimetric determination of iodate.

Reagent. Pyrogallol solution: Dissolve 5 g. of pyrogallol in 25 ml. of 0.1 N sulfuric acid and dilute to 100 ml.

Standard potassium iodate solution: Dissolve 0.1 g. of pure potassium iodate in water and dilute to 1 liter.

Procedure. To 20 ml. of unknown solution, add 0.5 ml. of reagent and mix well. Allow to stand for 5 minutes and compare in a colorimeter with the standard which has been similarly and simultaneously prepared. The accuracy of this method is about 0.2 per cent.

Determination of carbon monoxide. Berger and Schrenk^{54,55} have used pyrogallol in a procedure for the detection and determination of carbon monoxide. This reagent is used in much the same manner as that described for tannin.

Determination of oxygen. Dobereiner⁵⁶ was the first to observe that oxygen is absorbed by an alkaline solution of pyrogallol. Liebig⁵⁷ applied this reaction to the quantitative removal of oxygen from air and mixtures with other gases. He found that 1 g. of pyrogallol in an ammoniacal solution absorbed 260 ml. or 0.38 g. of oxygen, and 1 g. of pyrogallol in potassium hydroxide solution absorbed 189 ml. of the gas.

Calvert^{58,59} and other investigators^{60,61,62} found that carbon monoxide is formed under certain conditions when an alkaline solution of the reagent is oxidized by oxygen. Boussingault⁶² used 5 ml. of a potassium hydroxide solution containing 2 g. of potassium hydroxide and 0.8 g. of pyrogallol, and found that 0.4-3.4 per cent of carbon monoxide was given off when oxygen acted upon the reagent.

Clowes^{63,64,65,66} found that carbon monoxide is given off unless an excess of potassium hydroxide is present. He found that a solution containing 10 g. of pyrogallol and 24 g. of potassium hydroxide to 100 ml. of solution can be used for the determination of oxygen when the latter does not exceed 28 per cent of the total volume of gas used. Carbon monoxide is formed by the analysis of richer mixtures. Clowes recommends that the quantity of potassium hydroxide be increased to 120 g. when gases contain more than 28 per cent oxygen. He claims that a solution prepared by dissolving 160 g. of potassium hydroxide and 10 g. of pyrogallol in 200 ml. of water does not give off carbon monoxide even when analyzing pure oxygen.

Lewes⁶⁷ states that a freshly prepared solution of pyrogallol should not be used, but that it should be allowed to stand for 24 hours after mixing. He used a solution of 10 g. of pyrogallol in 150 ml. of 20 per cent sodium hydroxide, and claimed that after this solution was used for some time carbon monoxide was given off. Berthelot^{68,69} states that pyrogallol, when mixed with more than 3 equivalents of potassium hydroxide, gives off carbon monoxide equivalent to 0.013 of the oxygen absorbed, and that absorption is constant between 15-62° C. when using from 1-3 equivalents. With 0.5 equivalents of potassium hydroxide, absorption of oxygen is reduced and the formation of carbon monoxide is increased. Berthelot^{68,69} recommends mixing 32 g. of pyrogallol in 100 ml. of water with 3 or more equivalents of potassium hydroxide.

Jones and Meighan⁶⁹ report that sodium pyrogallate solutions prepared by using sodium hydroxide solutions of sp. gr. less than 1.30 give off carbon

monoxide, which increases with dilution. Cold sodium pyrogallate solutions give off carbon monoxide when analyzing oxygen samples containing about 95 per cent oxygen. For a reagent which gives off a minimum of carbon monoxide and which has a fairly high rate of absorption, these authors recommend the following:

Reagent. Solution A: Dissolve stick sodium hydroxide in an equal weight of water.

Solution B: Prepare a solution of pyrogallol in the ratio of 1 g. of pyrogallol to 3 g. of water.

Procedure. When ready to use, mix 5 parts of sodium hydroxide solution with 2 parts of pyrogallol solution.

Haldane and Makgill⁷⁰ report that all alkaline pyrogallate solutions may give low results in determining oxygen in air, due to the formation of a little carbon monoxide. A solution prepared by dissolving 10 g. of pyrogallol in 100 ml. of 80 per cent potassium hydroxide does not give low results for oxygen in air if the mixture is allowed to stand for 3 days before it is used. Similar results are obtained by heating the mixture for 1 hour in a boiling water bath before using.

Weyl and Goth⁷¹ have studied the use of pyrogallol for the absorption of oxygen, and have concluded that the absorption of oxygen is at a maximum when a quantity of sodium hydroxide sufficient to form $C_6H_3(ONa)_3$ is used, but that this is not true when sodium hydroxide is replaced by potassium hydroxide. They recommend a reagent prepared by dissolving 0.25 g. of pyrogallol in 10 ml. of sodium hydroxide solution of sp. gr. 1.030. Weyl and Zeitler⁷² state that the maximum absorption of oxygen is obtained with a potassium hydroxide solution of sp. gr. 1.05, and that a solution of sp. gr. 1.50 is too concentrated.

Shipley⁷³ has made an exhaustive study of the use of sodium hydroxide as a substitute for potassium hydroxide in the pyrogallol reagent and he has concluded that sodium hydroxide is equal to or superior to the potassium compound. He claims that no carbon monoxide is given off and that the rate of absorption is proportional to the concentration of the reagent. He further states that ammonium and barium pyrogallates are impracticable.

Anderson^{74,75} claims that the solution used by Shipley is too viscous, and states that the saving due to the lower cost of the sodium compound is more than offset by the time consumed for complete absorption and the extra manipulation which the viscous solution entails. Ishisaka⁷⁶ also recommends the potassium salt.

Benedict⁷⁷ claims that results obtained in determining oxygen with pyrogallol depend upon the concentration of the alkali employed. Haldane¹⁰⁰ recommends a reagent prepared by adding 1 g. of pyrogallol to 10 ml. of potassium hydroxide solution having a sp. gr. of 1.55. A comparative summary of oxygen reagents used by various authors is given in Table 30. Various other formulas have been proposed.⁸⁴⁻⁹⁰

TABLE 30.—COMPOSITION OF ALKALINE PYROGALLATE SOLUTIONS

Author	g. per 100 ml. of Solution		Reference
	Reagent	Potassium Hydroxide	
Leibig	6-7	37	
Clowes (a)	10	24	
(b)	10	120	
Winkler	5	22	78
Hempel	3.5	84	79
Berthelot	15	25	80
Franzen	8	70	81
Gill (a)	4.9	43	82
(b)	4.9	81	
Haldane	9.4	74	
Benedict	9.4	66	83

Mackey and Middleton⁹¹ have used pyrogallol for the colorimetric determination of dissolved oxygen in water. A brown color is obtained when water containing dissolved oxygen is added to a solution of pyrogallol in potassium hydroxide, and this can be estimated by comparing with standard solutions containing known quantities of oxygen. Hamilton⁹² recommends the use of caramel solutions as permanent standards. Such solutions remain unchanged for several weeks.

Ambler⁹³ has also used an alkaline solution of pyrogallol for the rapid colorimetric determination of oxygen. This method is based on the brown color imparted by oxygen to an alkaline solution of pyrogallol, but the color is compared with that of an iodine solution of known strength. The method is suitable for quantities of oxygen ranging from 0.01-0.5 per cent and requires only 20 ml. or less of the gas. The gas to be analyzed is passed through the reagent solution, and after all oxygen has been absorbed the color is matched by running a 0.1 N iodine solution (containing 2 parts of potassium iodide and 1 part of iodine) dropwise into a cylinder similar to that containing the pyrogallol solution until the colors match. The amount of oxygen in the unknown can easily be determined after standardizing the iodine solution against gases containing known quantities of oxygen.

Forster⁹⁴ and Munroe⁹⁵ describe satisfactory methods using pyrogallol for high school determinations of oxygen in air.

A colorless alkaline solution of pyrogallol serves as a sensitive test for oxygen, since as little as 0.008 per cent of oxygen by volume is sufficient to impart to the solution a brown color.⁹⁶ Pyrogallol and potassium hydroxide solutions are united in a special apparatus after most of the air has been removed by suction and the remaining air displaced by evaporation of water. The gas to be analyzed is then introduced into the vessel, whereupon a brown or violet color appears if oxygen is present. Nitrogen, hydrogen, ethylene, carbon monoxide, nitrous oxide, nitric oxide and ammonia do not interfere with this

test, but carbon dioxide, sulfur dioxide, hydrogen sulfide, hydrogen cyanide, acetylene, chlorine and bromine interfere.

Determination of boron. Mellon and Morris⁹⁷ have studied the use of pyrogallol in the titration of boric acid, but report that it is not suitable for this purpose.

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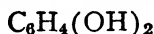
RESORCINOL

Synonym: Resorcin, m-dihydroxybenzene



Mol. Wt. 110.11

Beil. Ref. VI, 796.



Use: Detection of ammonia arsenic, cadmium, chlorate, columbium, gold, hyponitrous acid, lead, nitrate, nitrite, platinum, tantalum, titanium, tin, uranium and zinc.

Determination of cobalt, nitrate, nitrite, sodium and zinc.

Resorcinol consists of white needle-like crystals. These have a slight odor. The compound becomes pink on exposure to light and air or by contact with iron. It has a sp. gr. of 1.272 and melts at 109-110° C. It boils at 280° C., but volatilizes at a lower temperature and is slightly volatile in steam. One gram of the solid dissolves in 0.9 ml. of water, 0.2 ml. of hot water, and 0.9 ml. of alcohol. It is quite soluble in ether; but is only slightly soluble in chloroform.

Resorcinol reacts with the salts of a number of metals to yield color reactions which are useful in the analysis of these metals.¹ Lavoye² has studied the color reactions of a number of cations with resorcinol and recommends the following procedure:

Procedure. Add 1 ml. of a 10 per cent solution of resorcinol to 1 ml. of a dilute solution of a metallic salt and add 2 ml. of a 10 per cent solution of

ammonia. Warm for just an instant and allow the mixture to stand. The following color reactions are observed:

Ion	Reaction
✓ Zinc	Yellowish-green, greenish-blue and finally intensely blue.
✓ Cadmium	A blue color but less intense than that with zinc.
✓ Manganese	A deep blue-green color.
✓ Nickel	An intense bluish-green color.
Cobalt	A violet color tinged with blue.
✓ Copper	A deep blue color.
Platinum	A garnet-red color.
Arsenic	A sepia color.

Mercury salts produce no color effect, but the precipitate which forms on the addition of ammonium hydroxide dissolves in the presence of sufficient resorcinol.

When the colored solutions formed as described above are evaporated, deposits are obtained which are of the same color as the solutions. If a quantity of acid which is just sufficient to neutralize the ammonia is added to the solution, a red coloration is obtained in all cases.

Detection of zinc. The color reaction obtained with resorcinol and an ammoniacal solution of a zinc salt may be used for the detection of zinc.^{3-7,46} Resorcinol can be used in an aqueous or alcoholic solution or in ether. In the latter case the color is confined to the zone of contact of the ether solution of the reagent and aqueous solution of material to be tested, but with alcoholic or aqueous solutions the color develops throughout the entire liquid and consequently proceeds much more rapidly. If an aqueous solution of the reagent is used, heating the mixture to the boiling point causes the instantaneous production of a color. If the solution is boiled, however, care should be taken not to expel all ammonia. The solution should not be heated when an alcoholic or ether solution of the reagent is used. If the unknown solution is colored, an ether solution of resorcinol should be used in order to confine the color to the ether layer.

Procedure. Add dilute ammonia to the solution to be tested until the precipitate which forms just redissolves, and then add an aqueous, alcoholic or ether solution of resorcinol. With zinc, the color of the solution or the zone at the junction of the two liquids first appears yellowish, then green and finally blue. In this way 0.005 mg. of zinc can be detected in 1 ml. of solution. A faint yellow color is not considered a positive test.

Nickel salts give practically the same color reactions as zinc, and cobalt causes the characteristic yellowish color of the cobalt ammines. Manganese also interferes. Cadmium and copper and vigorous oxidizing and reducing agents interfere with the full development of the color. Aluminum and iron are without effect and so is chromium unless present in very large quantities.

The following modification of the zinc test is proposed by Fabich ⁸:

Procedure. Add a 10 per cent alcoholic solution of resorcinol to a dilute solution of zinc salt. A yellow color develops when this cold mixture is shaken and upon heating the color changes to an olive-green or blue, depending upon the concentration.

Other metals such as cadmium, nickel, cobalt, copper and manganese give similar colors.

Determination of zinc. Zinc may be determined colorimetrically by means of the blue color which is formed when ammonium hydroxide and resorcinol are added to a solution containing zinc ions.^{8,9}

Procedure. The sample used for the analysis should contain between 0.005 and 3 mg. of zinc. Dissolve in water, using acid if necessary, and add 6 N ammonium hydroxide drop by drop until the precipitate formed redissolves. Dilute to 100 ml. and add 2 ml. of a 5 per cent alcoholic solution of resorcinol. The blue color thus produced is matched against a standard prepared in the same way and containing approximately the same amount of zinc as the sample. The dilution method may be used, but is accurate only over a very narrow range. The method of duplication may also be used but other methods are not satisfactory.

The color reaction with zinc and resorcinol is sensitive to about 1 part in 100,000. The error observed for concentrations of zinc ranging from 0.1 to 3.2 mg. per 100 ml. varied from 0.06 to 6.6 per cent. The blue color of the reaction mixture is altered somewhat by exposure to air, and solutions should be protected with a layer of a suitable oil, such as Nujol, until ready for examination.

Solutions of zinc and hydrochloric acid are colored red by resorcinol and they are not altered by exposure to air, but a special comparison curve must be prepared using known amounts of zinc in the same way as the sample to be analyzed.

In ammoniacal solutions, calcium gives a green coloration with resorcinol, nickel a blue and cobalt a red color; hence, it is necessary to remove these metals before testing for zinc. Zinc borosilicate glassware must not be used.

The resorcinol method for determining zinc has been criticized as leading to false results. Mohler and Widmer ¹⁰ were able to produce, from an ammoniacal solution of resorcinol in anhydrous ether, crystals which upon exposure to air gave the same succession of colors and the same final blue color as in the colorimetric method for zinc. The color is produced in the absence of zinc, although salts of this element appear to hasten the development of the color.

Detection of cadmium. Bey ^{11,47} has proposed the following test for cadmium:

Procedure. Add ammonium hydroxide to a 5 per cent solution of resorcinol in ether dropwise until the precipitate which forms just dissolves. A solu-

tion containing only 0.0011 per cent of cadmium chloride added carefully to the above mixture gives a blue ring at the junction of two layers within 25 minutes. This color persists for 5-10 minutes. A non-characteristic violet color was obtained with a lower concentration of cadmium.

Detection of tin. Stannic tin may be detected by means of a color reaction with an ammoniacal solution containing resorcinol.¹¹

Procedure. Shake 2-3 ml. of a solution of stannic ion with 5 ml. of an aqueous solution of ammonia ($d = 0.925$) for several minutes. Then add 2-3 ml. of a 5 per cent aqueous solution of resorcinol. A white precipitate of stannic hydroxide is formed and this turns blue in 2-20 minutes. By means of this reaction an 0.0015 per cent solution of tin chloride can be detected. At a lower concentration of tin a non-characteristic gray precipitate is formed.

The tin test is not affected by less than 400 times as much antimony.

Determination of cobalt. Savari¹² has suggested a procedure for determining cobalt colorimetrically.

Reagent. Mix equal volumes of 0.05 M sodium nitrite and 0.05 M resorcinol and add 1 drop of 5 N hydrochloric acid. This solution should be freshly prepared.

Procedure. To 1 ml. of a solution containing less than 0.1 g. of cobalt per liter, add 2 ml. of the reagent and mix well. Add 1 drop of 5 N hydrochloric acid, mix, and add 5 ml. of 20 per cent ammonium thiocyanate solution. Shake 2 minutes in a separatory funnel with 5 ml. of ethyl ether, separate the red ether solution and compare it with a standard in a colorimeter.

Nickel, if present in quantities not exceeding 10 times as much as cobalt present, does not interfere.

Detection of lead. Lead, preferably as lead nitrate, reacts with resorcinol in an ammoniacal solution to yield a bright blue color.^{13,48} This reaction may be used for the detection of lead, although the color develops rather slowly. The following test is described by Miller¹³:

Procedure. Add 10 ml. of a 20 per cent alcoholic solution of resorcinol to 100 ml. of the solution to be tested, and add an excess of 1:1 ammonia. Cover the solution with an inert oil such as Nujol and allow to stand overnight if the color is slow in developing. As little as 1 part of lead in 1,000,000 parts of solution can be detected.

Colored ions interfere by masking the color developed in the reaction with lead. Zinc and cadmium also yield blue colors with resorcinol, but the shade is considerably lighter than that with lead. Barium, magnesium, silver, mercury, aluminum, the alkaline earths and the alkali metals do not interfere, and the distinctive blue color produced by lead may be observed even in the presence of small quantities of copper, nickel and cobalt. The test is most suitably applied to the detection of traces of lead in water and inorganic matter after the destruction of the organic material.

The following procedure has been suggested by Bey and Faillebin:¹⁴

Procedure. Add a little of the solution containing the lead salt to 5 ml. of 0.75 N ammonium hydroxide solution and allow to stand for a few minutes with occasional shaking. Mix with 5 ml. of 5 per cent resorcinol solution. A blue color gradually develops if lead is present. The sensitivity of this reaction is 30 mg. of lead per liter.

The slowness with which the color develops, and the fact that the tint varies with the condition of the test, limits the usefulness of this reaction.

Detection of uranium. Resorcinol and higher phenols react with yellow solutions of uranium salts to give colors varying from bright- to purple-red according to the concentration of uranium. These reactions may be used for the detection of uranium.¹⁵

Detection of platinum. Platinum can be detected by a color reaction obtained by treating a solution of a platinum salt with an ammoniacal solution of resorcinol and reducing with stannous chloride.¹⁶

Detection of titanium. Phenols react with concentrated solutions of titanium oxide in hydrochloric or sulfuric acids to yield a deep red or violet color.^{20,50,61}

Detection of gold. Resorcinol may be substituted for hydroquinone for the reduction of gold salts. Gold may be quantitatively recovered by means of this reaction. The use of resorcinol, however, seems to offer no special advantages over other reducing agents.¹⁷

Determination of sodium. Sodium may be determined by a procedure suggested by Barreto.¹⁸

Reagent. Heat 100 g. of resorcinol and 500 ml. of concentrated sulfuric acid to 120-125° C. for 1 hour.

Procedure. Treat a 20 per cent solution of a mixture of sodium chloride and potassium chloride with the reagent in the cold, using 25 ml. of the reagent for each gram of the mixed salt. The sodium salt is precipitated, and is washed with the reagent, alcohol and finally with ether. The precipitate is sodium resorcinolate.

Detection of columbium and tantalum. Resorcinol has been suggested as a reagent for the detection of columbium and tantalum.¹⁹ According to Zvyagintsev and Namoradze²¹ and Shemyakin and Pilipenko,²² however, K_2CbF_7 and K_2TaF_7 do not give characteristic color reactions with resorcinol in alkaline solutions as distinct from the blue-green or green-yellow reactions of resorcinol alone with ammonium hydroxide and potassium hydroxide. Resorcinol reacts with salts of cerium, thorium, praseodymium, lanthanum, zirconium and uranium in ammoniacal solutions to form bluish-green precipitates which differ but little in shade. If potassium hydroxide is substituted for ammonium hydroxide, yellowish and gray precipitates are formed.

Detection of ammonia. A reagent prepared by dissolving 2 g. of sodium nitroprusside and 1 g. of resorcinol in sufficient water to effect solution can be used for detecting ammonia in air.²³ For the test, a drop of the reagent is exposed on a white porcelain tile to the gas suspected of containing ammonia. A green or bluish-green color appears if ammonia is present. Volatile amines give the same reaction.

Detection of hyponitrous acid. Resorcinol may be used in a test for hydroxylamine or hyponitrous acid.²⁴

Reagent. *Resorcinol reagent:* Mix equal parts of 0.2 M resorcinol and a saturated solution of potassium periodate.

Buffer solution: Mix 21 g. of citric acid, 200 ml. of N sodium hydroxide and sufficient water to make 1 liter of solution.

Procedure. Add 4 ml. of buffer solution to 1 ml. of the solution to be tested, and then add 2 ml. of the freshly prepared resorcinol reagent. A cherry-red color develops within 3-15 minutes if either hydroxylamine or hyponitrous acid is present at a concentration of 1 p.p.m.

Rao⁵² claims that a similar test is obtained with nitrite.

Detection of chlorates. Chlorates may be detected by the green color formed when a solution of resorcinol in dilute sulfuric acid is added to a cold solution of a chlorate.²⁵

Fixing agent in the Kjeldahlization of nitrates.²⁶ When an alkali nitrate is treated with resorcinol, sulfuric acid and potassium sulfate and heated, the conversion of nitrogen to NH_4HSO_4 is complete. Phenol is not satisfactory for this purpose.

Detection and determination of nitrites and nitrates. Nitrites may be detected by the color reactions obtained by treating acid solutions of nitrites with resorcinol. Wilson²⁷ tested sulfuric acid for nitrites by adding a very small quantity of resorcinol to a mixture prepared by diluting 1 ml. of the suspected acid with 5 ml. of water. A more or less intense yellow color was produced according to the quantity of nitrous acid present. A modification of this test, proposed by Deniges,²⁸ may be carried out as follows:

Reagent. Dissolve 1 g. of resorcinol and 10 drops of sulfuric acid in 100 ml. of water.

Procedure. Mix 10 drops of the liquid to be tested with 2 ml. of concentrated sulfuric acid and add 5 drops of the reagent. A carmine-red to violet-blue color is obtained if nitrites are present.

Lindo²⁹ has proposed a somewhat similar test for nitrates.

Procedure. Add 1 drop of hydrochloric acid and 1 drop of a 10 per cent aqueous solution of resorcinol to 0.5 ml. of the solution to be tested and add 2 ml. of concentrated sulfuric acid. A purple-red color forms if nitrate is present. This reaction is sensitive to 1 p.p.m. of nitrate.

Rodillon^{30,31,32} has suggested an adaptation of the Wilson test for the detection of nitrites in water.

Reagent. Dissolve 3 g. of resorcinol in 50 ml. of concentrated sulfuric acid.

Procedure. Float the water to be tested over the reagent and observe the color which appears at the zone of contact between the two liquids. A rose-red ring or zone underneath the water layer indicates nitrites.

Leffman³³ has used the procedure of Rodillon, but claims that he was unable to obtain consistent results. According to Heller³⁴ this was due to the use of hot sulfuric acid for dissolving the resorcinol. If a cold acid is used and the reagent is freshly prepared for each test, trustworthy results are claimed. When the reagent is allowed to stand for some time a crystalline deposit is formed and the solution becomes useless. The following procedure is suggested by Heller.

Procedure. Shake 0.4 g. of resorcinol with 5 ml. of cold concentrated sulfuric acid, and carefully pour 1 ml. of this solution below the surface of 5 ml. of water to be tested. A green-violet or blue color, according to the concentration of the nitrite, appears at the interface between the two liquids.

Heller claims that the reagent solidifies after about 8 hours, and for further use it is necessary only to add a few drops of warm water and warm the mixture until the crystalline solid is dissolved. Leffmann³⁵ claims again, however, that he was unable to liquefy the resorcinol reagent which had previously solidified. Further, he claimed that the resorcinol test is inferior to the sulfanilic acid- α -naphthylamine test, and the test employing *m*-phenylenediamine.

When a nitrate or nitrite is treated with concentrated sulfuric acid, nitrosyl sulfuric acid is formed, and this compound reacts with phenols such as resorcinol, phenol, and thymol to yield strongly colored compounds. This reaction has been used by Eichler³⁶ for the detection of nitrites, nitrates, or nitrosyl sulfuric acid.

Procedure. To a small quantity of nitrate or nitrite add 1-2 ml. of a solution of 0.5-0.6 g. of resorcinol in 100 g. of sulfuric acid (free of nitrosyl sulfuric acid). When any effervescence has subsided, heat until a violet coloration appears, or until sulfur trioxide is evolved. Cool, dilute with 5-10 ml. of water, and neutralize with sodium carbonate. A violet color indicates nitrate or nitrite.

To detect nitrate in the presence of nitrite, adjust the pH of solution to about 3.0, and evaporate the mixture to dryness with ammonium chloride and test as above.

Ferric ions, sulfides and oxidizing agents interfere. If these substances are present it is best first to heat the material for some time with concentrated sulfuric acid, add solid resorcinol to the cold acid mixture until a blue coloration is produced, and heat until a violet color appears. In some cases oxidizing agents can be removed by precipitating with lead acetate.

The following modification of the resorcinol test for nitrite has been proposed by Ware:⁸⁷

Procedure. Mix 2 ml. of the aqueous solution with 0.05 g. of resorcinol and carefully pour 3 ml. of nitrogen-free sulfuric acid down the side of the tube. Shake lightly and allow the mixture to stand for 2 minutes, and then add 5 ml. of water. Finally, add 5 ml. of the mixture to 5 ml. of cooled concentrated ammonium hydroxide. Ammonia must be in excess. A rich scarlet fluorescence appears if nitrites are present. A wine-purple color is obtained at a dilution of 1:100,000, a purple-violet color at 1:50,000, and a blue-violet color at 1:20,000.

The intensity of the color produced in this reaction may be used for the estimation of small quantities of nitrites by comparing with that produced in solutions of known nitrite content.

The color reaction produced by concentrated sulfuric acid and various oxidizing agents has been studied by Korenman.⁸⁸ These studies reveal that the heat produced by the action of the acid and water influence the intensity of the color. If no oxidizing agent is present, the intensity of the color increases with a rise in temperature independently of the concentration. The reverse is true when an excess of an oxidizing agent is present. This is probably due to the fact that the colored substance is destroyed by the oxidizing agent. Further, each color appears to have an optimum temperature. As ordinarily carried out the tests do not take place under uniform temperature conditions with the result that colorimetric comparisons based upon such reactions are often inaccurate. According to Korenman⁸⁸ this is true of determination of nitrite employing color reactions with resorcinol.

Adler³⁹ has used the Wilson²⁷ reaction for the detection of nitrites in urine. Urine is treated with a small quantity of resorcinol and a little concentrated hydrochloric acid and then boiled. A red color which is changed to violet by the addition of a slight excess of ammonia indicates the presence of nitrite.

Ekkert⁴⁰ has studied the reaction between nitrites and nitrates and resorcinol, and reports the following color reactions: When 0.1 g. of sodium nitrite is added to 5-6 ml. of 33 per cent hydrochloric acid containing 0.02-0.03 g. of resorcinol, an immediate saffron-yellow color appears. This later changes to a reddish-brown and finally to a dark mulberry-red, and, after 20-25 minutes, and upon adding 0.02 N sodium hydroxide, becomes dark green. A portion of the green liquid when shaken with methyl acetate colors the methyl acetate violet-red. Another portion imparts a rose to eosin-red color to ethyl acetate. A third portion when diluted with water turns violet or lilac and eventually green. These solutions show a fiery-red fluorescence with reflected light. If the test solution contains more resorcinol than that indicated above, and an alkali is added after 5 or 10 minutes, a dark blue color develops and this gradually changes to green. When the mixture is diluted with water, a blue color with a red fluorescence appears.

When 5-6 ml. of 33 per cent hydrochloric acid containing 0.02-0.03 g. of resorcinol is added to 0.01 g. of potassium nitrate, only a pale yellow color appears after 5 minutes. Upon heating in a boiling water bath, however, the

solution immediately becomes yellow, then peach-red and finally dark mulberry-red. Upon cooling and adding sufficient 0.2 N sodium hydroxide the solution becomes dark green. Methyl acetate is colored violet-red and ethyl acetate is colored rose-red.

Other oxidizing agents such as potassium chlorate cause an immediate green to red-brown color with a hydrochloric acid solution of resorcinol. Bromates cause a reddish-brown color, iodates a greenish-brown color and dichromates a dark green.

Vagi⁴¹ has modified the original Wilson reagent by dissolving 1 g. of resorcinol in 400 ml. of 25 per cent acetic acid. This reagent gives a yellow color with nitrites, and may be used for the colorimetric determination of nitrites at a concentration of 1-5 mg. of N_2O_3 per liter.

Castiglioni⁴² recommends using solid resorcinol or its alcoholic solution for detecting nitrites. A yellow color is obtained when an alcoholic solution of resorcinol is added to an aqueous solution of nitrite. This changes to an orange-red when heated.

Novelli^{43,44} has used a reagent containing resorcinol and ferric chloride for the detection of nitrites.

Reagent. Dissolve 5 g. of pure resorcinol in 150 ml. of distilled water, and add 5 drops of 26 per cent ferric chloride solution. An intense violet color appears, and upon boiling this slowly fades leaving a yellow solution. Continue to boil for a few minutes and allow the solution to cool.

Procedure. Place a few drops of the solution to be tested in a test tube and add 1-2 drops of acetic acid free from nitrous acid. Add a few drops of the reagent. An intense green color develops if nitrites are present.

By using 100 ml. of solution, 1 part of nitrous acid in 10,000,000 parts of solution can be detected. Mineral acids, alkalies and vanadium interfere, the latter in concentrations as low as 1:10,000.

Alvarez^{45,49} has used a resorcinol reagent containing diphenylamine for the detection of nitrites and nitrates.

Reagent. Dissolve 0.1 g. of diphenylamine and 0.1 g. of resorcinol in 10 ml. of concentrated sulfuric acid.

Procedure. Add 5-6 drops of reagent to 1 mg. of the substance suspected of being a nitrate or nitrite. A yellowish-green color with a blue margin is formed if the unknown was a nitrate. An orange-yellow solution is formed upon adding alcohol. Under the same conditions, nitrite yields a deep blue color with a red margin and the mixture dissolves in alcohol with the formation of a red solution.

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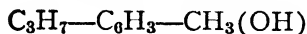
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THYMOL $C_{10}H_{14}O$

Synonym: 5-Methyl-2-isopropylphenol

Mol. Wt. 150.21

Beil. Ref. VI, 532.

**Use:** Detection of ammonia, antimony, arsenic, nitrate, nitrite and titanium.

Determination of ammonia, sulfate and titanium.

Thymol consists of colorless, translucent crystals which have a characteristic odor and pungent somewhat caustic taste. The compound melts at 51° C. and boils at about 233° C. One gram of the solid dissolves in about 1 liter of water, 1 ml. of alcohol, 0.7 ml. of chloroform and 1.5 ml. of ether. It is highly soluble in glacial acetic acid and the alkali hydroxides.

Detection and determination of titanium. Levy,¹ while studying the color reactions of titanic, columbic, tantalic and stannic acids, found that certain organic compounds containing one or more phenolic groups gave deep colorations with these acids. The reactions were carried out in concentrated sulfuric acid solutions, and Levy observed that with the exception of stannic tin the color was destroyed upon the addition of small quantities of water. This reaction was also studied by Hall and Smith.^{2,3}

Titanium reacts with thymol in concentrated sulfuric acid to give a deep red color, or a reddish-yellow color when small quantities of the metal are present. The color is proportional to the titanium content of the solution. This reaction has been used by Lenher and Crawford^{4,5} for the colorimetric determination of small quantities of titanium. Thymol produces the most satisfactory coloration for the estimation of small quantities of titanium. The intensity of the color produced is at least 25 times as great as that obtained using the hydrogen peroxide method.

Reagent. *Thymol reagent:* Dissolve 5 g. of thymol in 5 ml. of dilute acetic acid, and add 95 ml. of concentrated sulfuric acid. Mix well. Protect this solution from direct sunlight.

Standard titanium solution: This solution may be prepared from pure titanium dioxide or from a standard ferro-titanium steel. Dissolve 0.1 g. of pure titanium dioxide (or an equivalent quantity of standard steel) in a little sulfuric acid and dilute to 1 liter with concentrated sulfuric acid. One ml. of this solution contains 0.1 mg. of TiO_2 . This solution may be diluted with concentrated sulfuric acid if necessary.

Procedure. Dissolve a sample containing 1-10 mg. of TiO_2 in concentrated sulfuric acid; or, if necessary, fuse with potassium acid sulfate for one-half hour and dissolve the fused mass in concentrated sulfuric acid. Transfer the mixture to a Nessler tube and add the thymol reagent in such quantity that at least 60 mg. of thymol is added for each mg. of TiO_2 . Dilute to the mark with concentrated sulfuric acid. Add the same relative quantity of thymol to a measured volume of standard titanium solution and compare the color of the sample with that of the standard by the balancing method.

A series of standards containing varying quantities of TiO_2 may be used. If the dilution method is used, the dilution must be made with sulfuric acid of at least 80 per cent strength. The concentration of sulfuric acid in both sample and standard must be at least 79.4 per cent; otherwise the color obtained with the thymol reagent will be paler than the normal intensity.

The ratio of thymol to titanium can vary over wide limits, but best results are obtained with at least 60 mg. of thymol for each mg. of TiO_2 .

The color comparison must be made with solutions at room temperature. The color fades when the solution is heated, but returns to its original intensity upon cooling to room temperature, provided the mixture was not heated to 100°C .

Fluorides and hydrofluoric acid interfere by bleaching the thymol-titanium solution. Chlorides, phosphates and tin are apparently without effect upon the determination. Tungstic acid, however, exercises a very marked effect upon the color reaction.

Detection and determination of ammonia. When thymol is oxidized in the presence of ammonium salt, a dye is formed which is readily soluble in ether and xylene. This reaction has been used by Hansen ^{6,7,8} and by Lapin and Hein ⁹ as a color test for ammonia.

Reagents. *Thymol solution:* Prepare a 25 per cent solution of thymol in ethyl alcohol.

Sodium hypobromite solution: Mix 25 ml. of 2 N sodium hydroxide solution with 50 ml. of saturated bromine water.

Procedure. Add 1 ml. of the thymol solution to 5 ml. of the solution to be tested and add 12-15 ml. of the hypobromite solution. Allow to stand 1-2 minutes and add 5 ml. of ether or 3 ml. of xylene. Carefully invert the tube and turn back again several times. If ammonia is present a deep red to violet color appears in the organic solvent.

This reaction is also given by glycine and certain aliphatic amines. The above test may be used to detect 0.01 mg. of ammonia in 100 ml. of solution and is therefore less sensitive than the Nessler test under ideal conditions, but it is more generally applicable and is far superior to the odor test with sodium hydroxide.

Veinberg ¹⁰ has used thymol in a colorimetric method for the rapid determination of nitrogen and steel. This is an application of the method of Fue-Chan-Shi and Go-Nii-Kun ¹¹ for the determination of nitrogen in steels. This is based on the color reaction obtained by the oxidation of ammonium chloride or ammonium sulfate (formed by the decomposition of nitrogen steels in hydrochloric or sulfuric acid) with sodium hypobromite in the presence of thymol and the extraction of the resulting colored compound with ether or xylene.

Detection of nitrites and nitrates. By treating a nitrite or nitrate with concentrated sulfuric acid, nitrosyl sulfuric acid is formed, and this gives strongly colored compounds with various phenols. Eichler ¹² has used thymol to replace resorcinol in the detection of nitrites and nitrates (page 181).

Detection of antimony and arsenic. Ekkert¹³ has investigated a number of color reactions of phenols and has found that a chloroform solution of antimony pentachloride gives a brownish yellow to red-brown color with thymol. A mixture of 0.01 g. of thymol, 3 drops of sulfuric acid and 0.01 g. of sodium arsenate gives upon heating a scarlet-red, rose-red, violet and finally black-violet color.

Determination of sulfate. Kahn and Lieboff¹⁴ have determined sulfate by first precipitating with benzidine, then diazotizing the amine, and finally coupling the diazo compound with phenol to form a dye which is used for the indirect colorimetric estimation of the sulfates. Cuthbertson and Tompsett¹⁵ have proposed a similar procedure in which thymol is substituted for phenol as the coupling compound. A red color is obtained, which is more intense than the yellow color with phenol. For details of this procedure, see section on benzidine.

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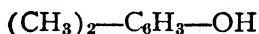
1,2,4-XYLENOL

Synonym: 1-Hydroxy-3,4-dimethylbenzene

$C_8H_{10}O$

Mol. Wt. 122.16

Beil. Ref. VI, 480.



Use: Detection and determination of nitric acid.

1,2,4-Xylenol is a colorless solid melting at 62.5° C. and boiling at 225° C. It is soluble in water and ethyl alcohol.

Detection and determination of nitric acid. 1,2,4-Xylenol is easily nitrated in the presence of sulfuric acid, and the resulting nitroxymol is volatile with steam. If the steam distillate is collected in an aqueous solution of an alkali hydroxide, a soluble colored compound is obtained. Blom and Treschow¹ have used this reaction for the determination of nitrates. Many other anions interfere, but by taking suitable precautions it is possible to prevent this interference. The following method proposed by Werr² may be used for the detection of nitric acid.

Procedure. Dissolve 0.1 g., or 0.1 ml. of the substance to be tested in 100 ml. of water and filter if the solution is not clear. To 1 ml. of this solution add a mixture of 5 ml. of 75 per cent sulfuric acid and 1 drop of 1,2,4-xynol. Allow the mixture to stand at room temperature for 10-15 minutes in a small flask which is closed with a rubber stopper. Shake from time to time, and add 20 ml. of water. Add a little pumice or distillation beads, and distill the mixture through a water-cooled condenser at the rate of 10 ml. in 5 minutes. Collect the distillate in a tube containing about 2 ml. of 0.5 N sodium hydroxide. By holding the tube against a white background and looking vertically through the solution, 0.001 mg. of nitrogen as nitrate can be detected by the yellow color which forms. With larger quantities of nitrates a reddish-yellow or red color is obtained. A blank test should be carried out simultaneously.

Nitrites interfere with this test and must be removed. If hydrogen peroxide is present a slight deepening of the color may be observed.

Blom and Treschow¹ used the above reaction for the colorimetric determination of small quantities of nitrates in soil. They claim that about 0.05 mg. of nitrate can be determined with an accuracy of about 2 per cent. Alten and Weiland³ state that the method of Blom and Treschow¹ has the theoretical advantage over methods using phenolsulfonic acid in that only 1 nitration product is likely to be formed. The 1,2,4-xynol method is capable of good results under favorable conditions, which include the absence of organic matter (as from plant extracts), lead, manganese or halide salts. Small quantities of acetic acid, oxalic acid, phosphoric acid and ethyl alcohol are entirely harmless.

The following modification of the method of Blom and Treschow¹ has been recommended by Alten and Weiland:³

Procedure. Make the solution to be tested alkaline and evaporate to dryness in a flask. Add 0.2 ml. of 1,2,4-xynol and 50 ml. of cold dilute sulfuric acid which has been prepared by adding 5 volumes of concentrated sulfuric acid to 3 volumes of water. If the quantity of nitrogen pentoxide present is greater than 10 mg., increase the quantity of sulfuric acid in the proper proportion. Stopper the flask and shake well until the residue is detached from the flask. Heat on a sand bath at 50° C. with frequent shaking for 4 hours or allow to stand overnight. Allow to cool and pour the contents of the flask into a 500-750 ml. distilling flask and rinse the nitrating flask thoroughly with dilute sodium hydroxide and water until the total volume is 400 ml. Distill the mixture with a low flame into a 250 ml. volumetric flask containing 25 ml. of N sodium hydroxide solution. The receiver and contents should be kept cold. When the receiving flask is nearly filled with the distillate, turn off the water in the condenser to allow the condenser tube to become hot enough to drive over any adhering compound. Dilute the distillate to 250 ml. at 20° C. and compare in a colorimeter with a standard containing about the same quantity of nitrate and similarly treated.

Alten and Weiland³ have investigated the use of the 5-nitro-2,4-xynol which was recommended as a standard by Blom and Treschow,¹ but they report that with this method results totaling only 70-80 per cent of the theory are

obtained. Blom and Treschow¹ and Treschow and Gabrielsen⁴ claim that the 1,2,4-xylenol distillation method for nitrates is not capable of high accuracy in the presence of more than 25 mg. of plant material. Alten and co-workers⁵ report that excellent results are possible in the presence of as much as 1 g. of plant material under the following conditions:

Procedure. Nitrate 1,2,4-xylenol at room temperature in the presence of 25 ml. of 66 per cent sulfuric acid. Allow to stand 20 minutes, dilute with 60 ml. of water and distill 45 ml. into 0.2 N sodium hydroxide solution. Clarify the distillate by shaking with barium sulfate. In addition to yellow nitroxylenol, various colored organic compounds formed by the action of heat and concentrated sulfuric acid upon plant materials are also distilled. The intensity of the color originating from this source must be determined for each class of sample, and the effect upon the color of the nitroxylenol then properly compensated.

1. J. Blom and C. Treschow, *Z. Pflanzenernahr., Dungung Bodenk.* **13A**, 159-90 (1929); *C.A.* **23**, 4994 (1929);
2. F. Werr, *Z. anal. Chem.* **109**, 81-91 (1937); *C.A.* **31**, 5295 (1937).
3. F. Alten and H. Weiland, *Z. Pflanzenernahr., Dungung Bodenk.* **32A**, 337-48 (1933); *C.A.* **28**, 1629 (1934).
4. C. Treschow and E. K. Gabrielsen, *Z. Pflanzenernahr., Dungung Bodenk.* **32A**, 357-76 (1933); *C.A.* **28**, 1300 (1934).
5. F. Alten, B. Wandrowsky and E. Hille, *Bodenkunde u. Pflanzenernahr.* **1**, 340-8 (1936); *C.A.* **31**, 2125 (1937).

CHAPTER X

MISCELLANEOUS PHENOLIC COMPOUNDS

Many substituted phenols or enolic compounds have been used in analytical procedures. The more important of these are included in the following sections.

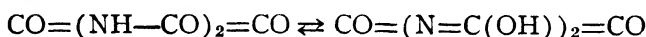
ALLOXAN

Synonym: Mesoxalylurea



Mol. Wt. 160.09

Beil. Ref. XXIV, 500.



Use: Detection of cadmium, cobalt, hydrogen cyanide, iron, magnesium, manganese, mercury, nickel, silver and zinc.

Alloxan is a white, crystalline solid, which becomes pink on exposure to air. It decomposes at about 170° C. It is freely soluble in water and alcohol.

Alloxan is an oxidizing agent and converts iodides to free iodine and indigo white to the blue compound. In general, the reactions of alloxan resemble those of the quinones.

Preparation of reagent solution. Treat 2 g. of uric acid with 2 ml. of nitric acid (sp. gr. 1.4) and after the reaction has ceased, add 2 ml. of water and heat to clarify the mixture. Then dilute with water to 100 ml.

Detection of hydrogen cyanide. Hydrogen cyanide may be detected by its catalytic effect in promoting the reaction between ammonia and alloxan to form characteristic crystals of oxaluramide. This reaction was first observed by Rosing and Schischkow,¹ and since then has been studied by Strecker² Deniges,^{3,4} and Kozlovskii and Penner.^{5,6} The test may be made as follows.^{3,7,8}

Procedure. Mix the substance to be analyzed with an equal weight of water, and allow to stand for 1 hour in a tall, narrow glass cylinder, on the end of which is a watch glass carrying, on its underside, a drop of the reagent described above. In the presence of hydrogen cyanide, a red coloration is observed.

The red color is due to the formation of murexide, caused by the action of dialuric acid (accompanying oxaluramide) on the excess of alloxan. Murexide is an ammonium salt of purpuric acid.

This test has been modified as follows:⁴

Procedure. One drop of 1:5 solution of ammonia is placed on a microscope slide, and this is inverted over a narrow tube containing the solution to be tested which has been mixed with a few drops of sulfuric acid. After a few minutes remove the slide and place under a microscope. On the addition

of a drop of alloxan solution (see above), crystals of oxaluramide begin to form if the solution tested contained hydrogen cyanide or a cyanide.

The substitution of pyridine for ammonia renders the test more sensitive. A few drops of a solution containing 0.01 g. of hydrogen cyanide per liter gives a positive test.

A critical study of this reaction has been made by Kozlovskii and Penner,^{5,6} who have used various amines instead of ammonia and pyridine. They report positive tests with ethyl amine, propyl amine, butyl amine, aniline, the toluidines, *p*-aminophenol, or *o*-anisidine. Butyl amine proved the most sensitive of those tested.

Reactions with metals. Deniges^{9,10} has studied the reactions which occur when a solution of the reagent is warmed with solutions of salts of a number of metals. The color reactions are reported in Table 31.

TABLE 31.

Metal	Color	Color after Addition of a Few Drops of Sodium Hydroxide
Zinc	Yellow to orange yellow	Carmine-red
Magnesium	Carmine red	Violet
Cadmium	Garnet-red	Carmine-red
Ferric iron	Yellowish-brown	Blue
Cobalt	Orange-yellow	Bordeaux-red
Nickel	Orange-yellow	Brown—then red
Manganese	Carmine-red	Blue-violet

A blue color is formed when a ferrous salt solution and a little sodium hydroxide are added to a solution of alloxan.

Dubsky, Keuning, and Sindelar,^{11,12} in a more recent study of the reactions of alloxan, report as follows:

(a) With lead acetate a white precipitate of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4\text{C}_4\text{HO}_4\text{N}_2 \cdot \text{H}_2\text{O}$ is formed.

(b) A gray precipitate is formed with mercuric acetate.

(c) A voluminous white precipitate is obtained with silver nitrate.

(d) A slight white precipitate appears with mercurous nitrate.

Alloxan does not, however, form precipitates with other cations. It does not precipitate ferrous salts, even after the addition of sodium acetate, or in the presence of ammonia. Ferric salts are not precipitated in slightly acid solutions, but solutions containing alloxan and ferric salts turn dark after the addition of sodium acetate.

In a recent review of the reagents used for the detection of manganese, Wenger and Duckert¹³ report unfavorably on alloxan, claiming that it is neither sufficiently sensitive nor specific to be of much value.

Previous misinterpretations of reactions of alloxan are, in the opinion of Dubsky and co-workers, due to the fact that alloxan can be reduced to alloxantin, and that alloxantin may be oxidized to alloxan. Consequently, many of the reactions ascribed to each of these substances individually, occur only when a mixture of the two is present.

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2. A. Strecker, *Ann.* **113**, 48, 53 (1860).
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13. P. Wenger and R. Duckert, *Helv. Chim. Acta.* **25**, 1143-50 (1942).
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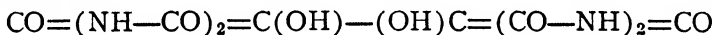
ALLOXANTIN

Synonym: Uroxin

$C_8H_6O_8N_4 \cdot 2H_2O$

Mol. Wt. 286.16

Beil. Ref. XXVI, 556.



Use: Detection and determination of iron.

Alloxantin is a white crystalline powder which, on exposure to air, becomes red. When heated to 225° it turns yellow. It decomposes at 253-255° C. It is sparingly soluble in water, alcohol and ether. The aqueous solution of this compound reacts acidic, reduces silver salts, and gives a blue precipitate with barium hydroxide solution.

Preparation. *Method (1):* Place 10 g. of pure uric acid in a 500-ml. flask and add 10 ml. of concentrated nitric acid. Heat, shake, and allow to stand 1-3 minutes, after which a vigorous reaction occurs with the evolution of nitrogen dioxide. When the reaction has subsided, add 10 ml. of distilled water and boil gently until solution is clear. Pour into the flask 200 ml. of distilled water, 1 ml. pure hydrochloric acid, and introduce a strong current of hydrogen sulfide for 30 minutes. The liquid becomes turbid with the formation of a yellow-white mass. Boil 10 minutes, filter, boil again, filter and collect the filtrate in a porcelain dish. Allow to stand for 2 days. Wash the crystals that have settled out several times with cold water, drain, and dry on filter paper.

Method (2): Place 15 g. of uric acid, 30 g. of concentrated hydrochloric acid, and 40 ml. of distilled water in a round bottomed flask. Heat the mixture to 30° C. and add in small portions over a period of 45 minutes 4 g. of potassium

chlorate. Filter, dilute with 30 ml. of water, and saturate with hydrogen sulfide. The precipitate which forms consists of alloxantin and sulfur. Filter and wash the precipitate with cold water, and then dissolve the alloxantin in boiling water. Filter off insoluble sulphur and cool the filtrate. Alloxantin separates in the form of prismatic crystals.¹

Detection and determination of iron. In a dilute ammoniacal solution, alloxantin reacts with ferrous salts to form dihydroxydiferrodialloxantin, which may adsorb or add 3 moles of ammonia and 13 moles of water.² This reaction has been used by Dubsky and co-workers^{2,3,4} for the detection of iron. The method is sensitive to 1.7 γ of ferrous salts at a dilution of 1:1765.

Alloxantin in an alkaline solution yields a blue color with ferric salts, and this reaction may be used for the detection of ferric ions.

Reagent. Dissolve 0.1 g. of alloxantin in 10 ml. of N sodium hydroxide. If a pink color develops (which should not appear with pure alloxantin), boil until the solution is colorless.

Procedure. Add 5 ml. of the above reagent to 10 ml. of the solution to be tested. A blue color develops if the solution contains as little as 1 mg. of ferric ion per liter.

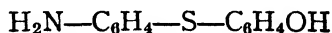
The test for ferric ion is successful even in the presence of salicylic, tartaric or citric acids, with which the well-known potassium thiocyanate reaction fails.⁵

Ferric iron may be determined colorimetrically by a method similar to that described above. One ml. of the reagent is added to 2 ml. of the ferric iron solution, and the resulting blue color is compared with standards similarly prepared.

Previous misinterpretations of the alloxantin reactions are due to the fact that alloxan can be reduced to alloxantin and vice versa; and the reactions ascribed to these substances by Liebig, Wohler, Mulder, and Deniges occurred only when mixtures of these two substances were present.²

1. G. Deniges, *Bull. soc. pharm. Bordeaux*, **66**, 8-12 (1928); *C.A.* **23**, 4160 (1929).
2. J. V. Dubsky, K. J. Keuning, and V. Sindelar, *Chem. Obzor.* **15**, 17-18 (1940); *C.A.* **34**, 6185 (1940).
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4. J. V. Dubsky, *Chem. Obzor.* **8**, 71-2, 93-5 (1933); *C.A.* **28**, 5361 (1934).
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4-AMINO-4'-HYDROXYDIPHENYL SULFIDE



Use: Detection of palladium and vanadium.

Detection of vanadium and palladium. 4-Amino-4'-hydroxydiphenyl sulfide reacts with the hypovanadous ion in concentrations as low as 0.2 mg.

per ml. By allowing the mixture to stand for 15-20 minutes the color may be observed in even more dilute solutions. The reagent also reacts with palladous salts to yield a bright yellow color. By comparing with a blank, this color may be detected in a solution containing as little as 5γ of palladium per ml. of solution.

1. W. E. Clark and L. K. Stallings, *Va. J. Sci.* 3, 31 (1942); *C.A.* 36, 3114 (1942).

2,5-BIS (2,4-DIMETHYL-N-PYRRYL)-3,6-DIBROMOHYDROQUINONE

$C_{18}H_{18}N_2O_2Br_2$

Mol. Wt. 454.15



Use: Detection of oxidizing agents, such as bromine, chlorine, ferric iron and ferricyanide.

2,5-Bis(2,4-dimethyl-N-pyrrolyl)-3,6-dibromohydroquinone is a colorless compound which is easily changed to a blue quinone by oxidizing agents.

Preparation: Mix a cold alcoholic solution of 8.6 g. of 2,4-dimethylpyrrole and 12 g. of 2,5-dibromoquinone in acetone and allow to stand for 1 day. About 8 g. of the reagent are obtained with this treatment.^{1,2}

Detection of oxidizing agents. 2,5-Bis(2,4-dimethyl-N-pyrrolyl)-3,6-dibromohydroquinone is readily oxidized to an intense blue quinone by oxidizing agents in such solvents as pyridine, ethyl acetate, dioxane or ethyl alcohol.^{1,2,3} This reaction is useful in showing organic peroxide formation in auto-oxidation reactions and polymerization processes, and in detecting inorganic oxidizing agents such as ferric iron, ferricyanides, chlorine and bromine. A 0.5-1.0 per cent solution of the reagent in pyridine is suitable as a reagent. In this way 0.002 mg. of ferric iron can be detected.

1. P. Pratesi, *Gazz. chim. ital.* 66, 215-23 (1936); *C.A.* 31, 1024 (1937).
2. P. Pratesi and R. Celeghini, *Gazz. chim. ital.* 66, 365-70 (1936); *C.A.* 31, 2543 (1937).
3. P. Pratesi and R. Celeghini, *Atti V Congr. nazl. chim. pura applicata*. Rome (1935), Pt. II, 847-9 (1936).

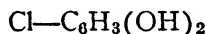
2-CHLOROHYDROQUINONE

Synonym: Adurol

$C_6H_5O_2Cl$

Mol. Wt. 144.56

Beil. Ref. VI, 849.



Use: Determination of dissolved oxygen.

This compound is obtained as leaves from chloroform. It melts at 106° C. It is very easily soluble in water, alcohol, and ether, but it is only very slightly soluble in cold chloroform.

Preparation: 2-Chlorohydroquinone is prepared by passing dry hydrogen chloride into a moderately concentrated solution of quinone in dry chloroform until the brown precipitate which first appears becomes white. Dry the precipitate in a desiccator over paraffin and potassium hydroxide, and then crystallize from chloroform.¹

Determination of dissolved oxygen. When dissolved in water, 2-chlorohydroquinone yields a brown color which depends on the amount of dissolved oxygen present. On standing, this color turns to a reddish brown. This reaction has been used by Winkler² as the basis for method for estimating dissolved oxygen colorimetrically.

Procedure. Place two samples of water in 50 ml. bottles. Saturate one sample with air by previously shaking in a large flask. Now add a small quantity of the reagent to each bottle, and then approximately 0.5 ml. of 10 per cent ammonium hydroxide containing 20 per cent ammonium chloride. The bottles are filled, stoppered and shaken. The amount of dissolved oxygen may be estimated by comparing the resulting color.

Winkler³ has found that a 2 N solution of sodium chloride dissolves only half as much oxygen as the same volume of distilled water at the same pressure and temperature. Such solutions may be used in the preparation of color standards.

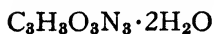
Winkler⁴ has used for the oxygen determination a reagent consisting of a mixture of dry powdered borax and 2-chlorohydroquinone. This determination, which is only approximate, is carried out as follows:

Reagent. Heat a quantity of borax for several hours at 50° C., and mix 6 parts of the borax with 1 part of 2-chlorohydroquinone and 3 parts of sodium potassium tartrate. The sodium potassium tartrate is used to prevent the precipitation of calcium and magnesium.

Procedure. Obtain a number of glass-stoppered bottles of uniform size and fill one with the sample and the others with the standards. Add to each about 0.5 g. of reagent for each 100 ml. of sample or standard. Stopper and invert several times to dissolve the reagent. Allow to stand 5 minutes until a reddish brown color develops. Estimate the oxygen content of the sample by comparing with standards. The color of the sample solution and standard must be about the same, since dilution is not satisfactory.

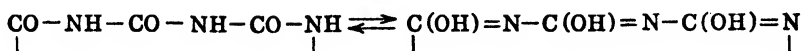
Standards are prepared by shaking water with air, allowing the bubbles to rise, and then diluting with known volumes of water that has been boiled and cooled in the absence of air. The solubility of oxygen in distilled water at 20° C. is 9.17 p.p.m.

1. S. Levy and G. Schultz, *Ann.* 210, 138 (1881).
2. L. W. Winkler, *Z. angew. Chem.* 24, 341 (1911); *C.A.* 5, 2054 (1911).
3. L. W. Winkler, *Z. angew. Chem.* 24, 831-2 (1911); *C.A.* 5, 2516 (1911).
4. L. W. Winkler, *Z. angew. Chem.* 26, 134 (1913).

CYANURIC ACID

Mol. Wt. 165.11

Beil. Ref. XXVI, 239

**Use:** Detection of manganese.

Cyanuric acid consists of colorless, shining crystals. It is slightly soluble in water but is almost insoluble in methyl alcohol, ethyl alcohol, ether, acetone, benzene and chloroform. It dissolves in concentrated sulfuric acid and in sodium hydroxide solutions.

Preparation: Dissolve 5 g. of uric acid in 200 ml. of water containing 9 g. of sodium hydroxide. Cool the mixture to 20° C., add 130 ml. of 3 per cent hydrogen peroxide, and allow the mixture to stand at room temperature for 24 hours. Filter, neutralize with a slight excess of hydrochloric acid and cool with ice water. Filter the crystals which form and concentrate the filtrate on a water bath to obtain additional crystals. Crystallize from hot water.^{1,2}

Detection of manganese. When a crystal of manganous sulfate is added to a few drops of a mixture of ammonium hydroxide and cyanuric acid, a white flocculent precipitate of manganous hydroxide forms. On boiling, or after standing for a few moments, this precipitate changes to colorless needles, formed in clusters, which possess great polarizing power.^{3,4} It has not been definitely established whether these crystals are chelate salts or unidentate coordination complexes. The precipitate is a manganous compound of cyanuric acid. If the manganese is first oxidized, no precipitate is formed. The reaction is very sensitive and can be used to detect manganese in the presence of zinc, cobalt, aluminum, nickel and chromium. To detect manganese in manganic compounds, simply dissolve in hydrochloric acid, heat, and then add cyanuric acid and ammonium hydroxide.

1. C. S. Venable and F. Moore, *J. Am. Chem. Soc.* **39**, 1750 (1917).
2. E. H. Walters and L. E. Wise, *J. Am. Chem. Soc.* **39**, 2472 (1917).
3. J. B. Menke, *Chem. Weekblad.* **15**, 868-9 (1918); *C.A.* **12**, 2173 (1918).
4. P. Wenger and R. Duckert, *Helv. Chim. Acta.* **25**, 1143-50 (1942); *C.A.* **36**, 3450 (1942).

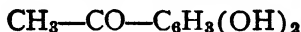
2,4-DIHYDROXYACETOPHENONE

Synonym: Resacetophenone



Mol. Wt. 152.14

Beil. Ref. VIII, 266 (613)

**Use:** Detection of boron and iron.

2,4-Dihydroxyacetophenone consists of leaves or needles, which melt at 143-144° C.

Preparation: Place 165 g. of glacial acetic acid in a 1-liter beaker, add 165 g. of anhydrous zinc chloride, and heat until solution is complete. To the hot mixture (140° C.), add 110 g. of resorcinol with constant stirring. Heat on a

sand bath until the mixture just begins to boil (about 152°C.) and then remove the flame. Allow the mixture to stand until the reaction is complete at a temperature not exceeding 159°. After 20 minutes on a sand bath without further heating, dilute with a mixture of 250 ml. of concentrated hydrochloric acid and 250 ml. of water. Cool in an ice bath at 5° C. and filter. Wash the precipitate free of zinc salts with 1 liter of 1:3 hydrochloric acid in 200-ml. portions. Dry and distill under reduced pressure. The compound distills at 180-181° C. at 10 mm. or at 142-152° C. at 3-4 mm. Discontinue the distillation when the temperature reaches 190° C. Remove the yellow distillate with ethyl alcohol and remove the alcohol by evaporation. Dissolve the compound in 1800 ml. of hot 1:11 hydrochloric acid, filter hot, and cool to 5° C. Filter, wash with two 200-ml. portions of ice water and dry. The pure compound melts at 142-144° C.¹

Detection of iron. Nencki and Sieber² first prepared 2,4-dihydroxyacetophenone and observed that it reacts with a solution of ferric chloride to produce a red color. This reaction has been used as a sensitive test for ferric ions.³

Procedure. Place 1.0 ml. of the solution to be tested on a colorless watch glass, and add 2 drops of a 10 per cent alcoholic solution of the reagent. Compare the resulting color with a blank obtained by adding 2 drops of alcohol to 1.0 ml. of the solution to be tested.

As little as 2 p.p.m. of ferric iron may be detected in this way, and this sensitivity compares favorably with that of the ferrocyanide and thiocyanate tests. Mercurous, mercuric, aluminum, and manganous ions give precipitates with this reagent, and chromium, cobalt, nickel and copper ions interfere because of their color. The solution to be analyzed may be 0.06 N in hydrochloric or nitric acids or 0.03 N in sulfuric acid.

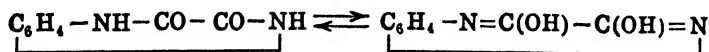
Detection of boron. A blue fluorescence appears in the presence of boric acid when 5 ml. of an alcoholic solution is treated with 10 mg. 2,4-dihydroxyacetophenone and an equal volume of syrupy phosphoric acid. No cations interfere, but chromate, bromate, chlorate, nitrite and fluoride interfere to a limited extent. In the absence of interfering ions, as little as 1 p.p.m. of boric acid gives a visible fluorescence.⁴

1. S. R. Cooper, *Organic Synthesis*, Vol. 21, p. 103.
2. M. Nencki and N. Sieber, *J. prakt. Chem.* [2] 23, 147 (1880).
3. S. R. Cooper, *Ind. Eng. Chem., Anal. Ed.* 9, 334-5 (1937); *C.A.* 31, 6130 (1937).
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2,3-DIHYDROXYQUINOXALIN

$C_8H_6O_2N_2$

Mol. Wt. 162.13 Beil. Ref. XXIV, 380(344).



Use: Detection of barium, calcium and strontium.

2,3-Dihydroxyquinoxalin is obtained as crystalline needles from water. It is soluble in boiling methyl alcohol and glacial acetic acid but is only slightly soluble in alcohol, ether and benzene. One liter of cold water dissolves 0.2 g. of the solid, while 1 g. dissolves in boiling water.

Preparation. 2,3-Dihydroxyquinoxalin is prepared by heating p-phenylenediamine with an excess of oxalic acid to 160° C. Crystallize the resulting product from boiling water or alcohol with animal charcoal.¹

Detection of barium, calcium and strontium. Barium, calcium and strontium are precipitated from solutions having a pH of 9.0-9.5 by means of 2,3-dihydroxyquinoxalin. Only the barium salt, however, is insoluble in strongly ammoniacal solutions. The barium compound corresponds to the formula $\text{Ba}(\text{C}_8\text{H}_5\text{O}_2\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$. The following procedure is used for the detection of barium:¹

Reagent. Prepare a saturated solution of the sodium salt of 2,3-dihydroxyquinoxalin by dissolving the reagent in boiling distilled water. Allow to cool and filter if necessary.

Procedure. To 0.5 ml. of the neutral or slightly ammoniacal solution to be tested (which has been filtered when calcium, strontium and barium have not been separated) add 1 ml. of concentrated ammonium hydroxide and 0.5 ml. of a cold saturated solution of the sodium salt of 2,3-dihydroxyquinoxalin. A white precipitate forms if barium is present. If the amount of strontium or calcium is several hundred times that of barium, add 2 ml. of ammonia instead of 1 ml. as recommended in the above procedure. This reaction is sensitive to 1 part of barium in 13,000 parts of solution.

The reaction for strontium or calcium, but not barium, can be made more sensitive by using a basic dye such as methylene blue or basic fuchsin in addition to the reagent.

Procedure. To 1 ml. of distilled water add 0.5 ml. of a cold saturated solution of the reagent and 0.2 ml. of a 1:5,000 solution of methylene blue in distilled water. Add the same quantities of the reagents to 1 ml. of distilled water as a blank. The presence of strontium or calcium is indicated by a color change from blue to blue-violet, followed by the precipitation of the dye. Barium does not cause a similar color change.

The above test may be made highly selective for calcium by using basic fuchsin instead of methylene blue. The color change in this case is from magenta (blank) to a violet if calcium is present. The sensitivity of the reaction is 1:55,000 using basic fuchsin and 1:18,000 for strontium when methylene blue is employed.

1. A. Steigmann, *J. Soc. Chem. Ind.* **62**, 42-3 (1943); *C.A.* **37**, 3689 (1943).

2,4-DINITRORESORCINOL

Synonym: 1,3-Dihydroxy-2,4-dinitrobenzene



Mol. Wt. 200.11

Beil. Ref. VI, 827.

**Use:** Detection of ferrous iron.

2,4-Dinitroresorcinol is a yellow crystalline solid. It melts at 146-8° C., and explodes when strongly heated. It is very slightly soluble in water or cold alcohol, but is soluble in solutions of alkali hydroxides.

Preparation: *2,4-Dinitroresorcinol:* Dissolve 1 mole of resorcinol in 50 times as much water and cool the mixture almost to 0° C. Then add 2 moles of acetic acid and 2 moles of potassium nitrite dissolved in water. Allow the mixture to stand 15 minutes and pour into a dilute solution containing 2 moles of sulfuric acid. Let stand 1 hour and filter, and recrystallize the precipitate from 50 per cent alcohol.

2,4-Dinitroresorcinol: Treat 2,4-dinitroresorcinol with 4 times as much nitric acid ($d = 1.3$) with cooling (1).

Detection of ferrous iron. 2,4-Dinitroresorcinol reacts with solutions of ferrous salts to form a greenish-blue coloration or precipitate.^{2,3} This reaction constitutes a sensitive test for ferrous ions.

Reagent. Dissolve sufficient 2,4-dinitroresorcinol in hot water to impart a brown coloration to the solution.

Procedure. Add a few drops of the reagent to a nearly neutral solution to be tested. With a trace of ferrous ions, a green coloration is obtained, but this becomes bluish with higher concentrations of the cation.

This test is said to be more sensitive than that with potassium ferricyanide. As little as 0.002 mg. of ferrous ion in 10 ml. of solution can be detected.

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3. G. Gutzeit, *Helv. Chim. Acta.* 12, 713, 829 (1929).

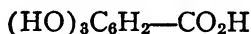
GALLIC ACID

Synonym: 3,4,5-Trihydroxybenzoic acid



Mol. Wt. 188.13

Beil. Ref. X, 470



Use: Detection of antimony, barium, bismuth, calcium, cerium, copper, dysprosium, erbium, lanthanum, lead, molybdenum, nitrite, praseodymium, silver, strontium, thallium, thorium, titanium, uranium, vanadium and yttrium.

Determination of bismuth, cerium, copper, nitrite, phosphorus, silver, thorium and titanium.

Gallic acid is obtained by fermenting an extract of gall nuts, or by boiling the extract with dilute sulfuric acid. It consists of white or pale grayish-brown crystals. The compound is usually obtained as the monohydrate, but it loses its water of hydration at 100-120° C. It melts at 240° C. with decomposition. One gram of the solid dissolves in 87 ml. of water, 3 ml. of boiling water, 6 ml. of alcohol, 5 ml. of acetone and 100 ml. of ether. It is insoluble in benzene and chloroform.

Separation and detection of antimony and bismuth. Gallic acid may be used for the separation of antimony and bismuth in the qualitative analysis of these metals.¹

Procedure. Add 3 ml. of a 2 per cent alcoholic solution of gallic acid to 3 ml. of the solution containing antimony and bismuth. A white turbidity appears, which increases on heating and turns a light yellow. This is basic bismuth gallate. Bismuth is completely precipitated by the addition of a few drops of water. The antimony salt which is formed simultaneously remains in solution. The mixture must not be diluted, since the soluble compound is less resistant to hydrolysis than the tartrate. A pH of 3 is suitable for the separation. Allow the mixture to stand, decant a portion of the liquid and centrifuge 2 minutes. Carefully remove by means of a pipet a quantity of the clear liquid for the antimony test. Rhodamine B is satisfactory for this purpose.

Das-Gupta² has used gallic acid to separate and detect bismuth in a scheme of analysis. In a nitric acid solution, bismuth is precipitated by gallic acid, while lead, copper and cadmium remain in solution. In a neutral or slightly acid solution containing sodium acetate, lead and copper are precipitated with gallic acid, whereas cadmium remains in solution. In a neutral or slightly acid solution, hydrogen peroxide and ammonium hydroxide precipitate lead but not copper. By making use of the above reactions an analytical group containing lead, bismuth, copper and cadmium can be separated with the use of gallic acid.

Separation and determination of bismuth. Kieft and Chandlee³ have reported that bismuth can be separated and determined in a 3 per cent nitric acid solution in the presence of lead, cadmium, copper, zinc, aluminum, chromium, iron, nickel, barium, calcium, sodium and potassium by precipitating with gallic acid. For a complete separation, it is usually necessary to dissolve the precipitate in nitric acid and reprecipitate with gallic acid.

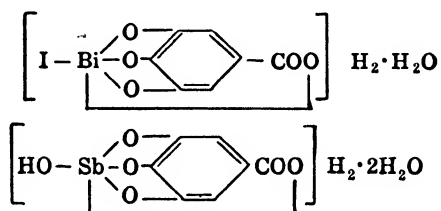
Procedure. Heat the solution of bismuth in 3 per cent nitric acid to 70° C. and add 50 ml. of a solution containing 1 g. of gallic acid. Stir for 1 minute and allow to cool. Filter and wash the precipitate by decantation. Stir for 1 minute. Cool, filter and wash the precipitate by decantation through filter paper, using 150 ml. of a solution containing 2 g. of gallic acid and 3 g. of ammonium nitrate in 100 ml. of water. Transfer the filter paper and precipitate to the original beaker, add 20 ml. of nitric acid, and heat to dissolve the precipitate and break up the paper. Filter off the paper, wash with 200 ml. of a 5 per cent nitric acid solution until free of bismuth, and then evaporate the filtrate to dryness. Add 10 ml. of nitric acid and 50 ml. of water and make

just alkaline with ammonium hydroxide. Then barely acidify with nitric acid and heat to 70° C. Reprecipitate with gallic acid. Use the same procedure as described above up to the point of addition of ammonium hydroxide. In the second precipitation, precipitate the bismuth as the subcarbonate and ignite to the oxide, according to the method of Scott.⁴

The solution containing the bismuth should not be heated above 85° C., since gallic acid begins to decompose and the decomposition products prevent the complete precipitation of bismuth. Bismuth gallate cannot be ignited to the oxide because of the ease with which the compound is reduced to the metal.

Mercury and antimony are partially precipitated with bismuth and tin also interferes. Silver is not completely removed with two precipitations.

Takagi and Nagase^{5,6} have studied the composition of antimony and bismuth precipitates with gallic acid and assign to them the following formulas:



The bismuth compound represented is formed in the presence of potassium iodide.

Determination of cerium. A qualitative test for cerium with alkaline pyrogallol⁷ has been modified by Shemyakin⁸ for the colorimetric determination of cerium with gallic acid. The product of the reaction between cerium, gallic acid and ammonium hydroxide is a light violet sol, which changes to a yellow-brown on standing, a similar sol which changes to green on standing, or a colorless sol depending upon the concentration of the reagents. Sodium thio-sulfate acts as a stabilizer for the sol.⁹ The recommended concentration for cerium is between 0.0002 and 0.00001 mole per ml. With higher concentrations the color becomes faint, and with 0.002 mole per ml. an amorphous bright-violet precipitate separates. The following procedure is recommended by Shemyakin:⁸

Procedure. Mix thoroughly 2.7 ml. of a 0.02 per cent gallic acid solution with 2.7 ml. of a cerium nitrate solution containing 0.03-0.07 mg. of cerium and then add 2 ml. of ether, toluene or mineral oil. Then introduce into the aqueous layer 5.3 ml. of a reagent prepared by dissolving 1 g. of crystalline sodium sulfate in 100 ml. of 0.1 M ammonium hydroxide solution. Mix carefully and dilute to 10 ml., so that the protective layer is above the mark. Compare the resulting color with that of standards similarly prepared.

The standard solution is prepared by dissolving 0.05 g. of ceric nitrate, $\text{Ce}(\text{NO}_3)_4$, in water and diluting to 1 liter. Each ml. contains 0.05 mg. of cerium.

Detection of rare earths. Shemyakin¹⁰ has studied the reactions of the rare earth salts and gallic acid in an ammoniacal solution. The results obtained

by adding a 1 per cent solution of gallic acid in an ammoniacal solution are shown in Table 32.

TABLE 32.

Metal	Reaction
Praseodymium	Yellow precipitate
Dysprosium	Yellow precipitate
Erbium	Rose precipitate
Yttrium	Yellow to rose precipitate
Cerium	Blue-violet precipitate
Thorium	Orange-red solution
Lanthanum	Brown solution

Detection and determination of thorium. Thorium may be detected by the orange-red color which is formed when a 1 per cent gallic acid solution is added to an ammoniacal solution of a thorium salt.¹⁰ Neish¹¹ has reported that gallic acid precipitates thorium quantitatively from a hot alcohol solution as a flocculent slimy precipitate. Salts of cerium, lanthanum and praseodymium and neodymium are not similarly precipitated.

Detection and determination of titanium. Solutions of titanium containing 1 mg. of titanium per ml. react with gallic acid to give a red-brown coloration.^{12,18} Smaller quantities of titanium give a yellow or greenish-yellow color. The color is deepened by the addition of sodium acetate. This reaction has been used by Das-Gupta¹⁴ for the colorimetric determination of titanium:

Procedure. Add 0.5 ml. of 1 per cent gallic acid solution and 0.5 ml. of 5 per cent ammonium acetate solution to 1 ml. of the solution containing titanium. Mix well and compare the resulting color with that of a series of standards.

According to Shemyakin⁸ results obtained with this method are as accurate as those using hydrogen peroxide. The reaction will detect as little as 1 p.p.m. of titanium.

Tungsten must be treated with perhydrol before the addition of gallic acid and the acetate. A light violet color is obtained. Molybdenum does not interfere if gallic acid is used in concentrated sulfuric acid, but under these conditions uranium, vanadium, columbium and ferric iron interfere.

Shemyakin and Neumolotova¹⁵ have studied the reaction of gallic acid with titanium and report that in mixing gallic acid with the titanium salt solution, the latter should at no time be mixed with sodium acetate solution unless gallic acid is already present. The optimum quantities of the reagent used in the determination are 8 ml. of 1 per cent gallic acid solution and 4 ml. of 5 per cent sodium acetate solution per 50 ml. of total volume of liquid. The solution should be neutral and should contain 0.1-0.5 mg. of titanium per ml.

Quantities of titanium ranging from 0.0003-0.08 mg. of titanium per ml. can be determined, and the method is reported to be 20 times more sensitive than

the hydrogen peroxide method. Iron, molybdenum, uranium, tungsten, chromium, cerium, aluminum, beryllium, thorium, zirconium, manganese, zinc, nickel, cobalt and calcium interfere and should be removed.¹⁵

Detection of molybdenum. Gallic acid reacts with molybdic acid to yield an orange to red color. This reaction is sensitive to 1 part of molybdenum in 100,000 parts of solution if the solution is neutral. Pozzi-Escot¹⁶ states that the intensity of the color is not proportional to the molybdenum content of the solution.

Determination of phosphorus. Passerini¹⁷ has used gallic acid for the colorimetric determination of phosphorus in soil and in rocks. The procedure consists of the following steps: precipitate phosphorus as the molybdate, wash, dissolve in ammonia and dilute to volume, treat with a cold saturated solution of gallic acid and compare the resulting yellow color with that of a series of standards.

Procedure. Boil 10 g. of the material to be analyzed for 1 hour with 30 ml. of concentrated nitric acid (40 ml. of nitric acid if the material contains considerable lime). Wash by decantation with boiling water, cool, and dilute the decanted liquid to 250 ml. Filter, evaporate 50 ml. of the filtrate to dryness and dissolve in nitric acid and boiling water. Dilute to 50 ml., filter off 25 ml. and treat with 2 ml. of 75 per cent ammonium nitrate solution and 25 ml. of molybdate reagent. Allow to stand for 24 hours and filter. Wash with 1 per cent nitric acid, dissolve in the least possible quantity of 1:3 ammonia and dilute somewhat. Boil to expel ammonia and dilute to 100 ml. Using a pipet, add this solution to a colorimeter tube containing 15 ml. of water and 2 ml. of a cold saturated gallic acid solution until the yellow color attains the same intensity as that in a similar tube to which has been added 1.5-2.0 ml. of standard phosphorus solution containing 1 g. P_2O_5 per liter.

Detection of vanadium. Gallic acid reacts with a solution of vanadic acid to give a blue color.¹⁸

Detection and determination of copper. Falciola¹⁹ has prepared a sensitive reagent for copper by adding an alkali thiocyanate solution to a cold saturated solution of gallic acid. This reagent gives a decided turbidity with a 0.0001 N copper sulfate solution, and a voluminous precipitate in more concentrated copper solutions. If a 0.00001 N copper sulfate solution is strongly agitated with a few ml. of the cold reagent, a perceptible white turbidity appears, especially if a large volume of the copper solution is used. The test must be carried out in neutral copper solutions, and in the absence of silver, lead and bismuth, which also yield precipitates with the reagent.

When a 1 per cent gallic acid solution is added to a boiling solution containing copper and cadmium and an alkali acetate, a voluminous brown precipitate is formed, which can be filtered and ignited to CuO . Cadmium is not precipitated under the same conditions.²⁰

Detection of uranium. A marked coloration is produced when gallic acid is added to a solution of uranium salt and followed with sodium acetate. This reaction is claimed to be more sensitive than the sodium salicylate test.²¹

Procedure. To a neutral solution of a uranyl salt, add 2 ml. of a 1 per cent gallic acid solution and 1 ml. of a 5 per cent sodium acetate solution. In 10 ml. of the test solution, uranium can be detected at a concentration of 23 mg. of uranium per liter. Gallic acid is superior to tannic acid or resorcylic acid.

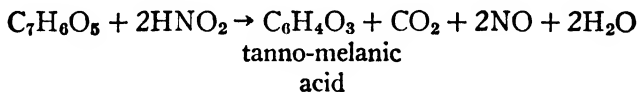
Detection and determination of silver. Costeanu²² has used filter paper impregnated with an alcoholic solution of gallic acid for the microchemical detection and determination of silver. Gallic acid is capable of reducing silver salts to metallic silver, and from the appearance of the spot, the amount of silver present can be approximately estimated. The spot produced by a drop of the unknown solution is compared with a series of standards prepared from drops of silver solutions of known concentration.

Detection of thallium. Shemyakin and Volkova²³ report that thallium hydroxide, $\text{Ti}(\text{OH})_3$, dissolves in gallic acid to yield a clear brown solution.

Detection of barium, calcium and strontium. Schweket^{24,25} has observed the color reactions which are obtained with gallic acid and solutions of the alkaline earth hydroxides. These reactions, however, seem to be of little analytical value.

Detection of lead. Gallic acid gives a very sensitive carmine-red color with an alkaline lead solution. Schweket²⁴ has recommended this reaction for the detection of traces of lead.

Detection and determination of nitrites. Davy²⁶⁻²⁹ has used gallic acid for the colorimetric determination of nitrites in water. This reaction is based upon the oxidation of gallic acid by nitrous acid according to the following equation:



By means of the resulting color reaction, 1 part of nitrite in 20,000,000 parts of solution can be detected readily. The color is unaffected by dilute sulfuric, nitric, hydrochloric or even concentrated solutions of the organic acids. Organic matter, nitrates and salts do not interfere. Iron, however, must be precipitated with ammonia:

Reagents. *Gallic acid solution:* The reagent is a saturated gallic acid solution which has been decolorized with charcoal and made strongly acid to prevent change of color.

Standard nitrite solution: Decompose 0.406 g. of silver nitrite with sodium chloride and dilute the solution to 1 liter. When clear, filter and dilute 100 ml.

of the filtrate to 1 liter. One ml. of the diluted solution contains 0.01 g. of N_2O_5 .

Procedure. To 25 ml. of the water to be analyzed add 1-2 ml. of the gallic acid solution and heat with a few drops of hydrochloric or sulfuric acid. Compare the resulting color with that of standards similarly prepared.

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20. P. N. Das-Gupta and H. Saha, *J. Indian Chem. Soc.* **8**, 19-21 (1931); *C.A.* **25**, 2938 (1931).
21. P. N. Das-Gupta, *J. Indian Chem. Soc.* **6**, 763-6 (1929); *C.A.* **24**, 1212-13 (1930).
22. N. D. Costeanu, *Mikrochemie.* **26**, 170-4 (1939); *C.A.* **33**, 3290 (1939).
23. F. M. Shemyakin and V. A. Volkova, *J. Gen. Chem. (U.S.S.R.)* **7**, 1553-56 (1937); *C.A.* **31**, 8421 (1937).
24. O. Schweket, *Biochem. Z.* **54**, 277-81 (1913); *C.Z.* **II**, 958 (1913).
25. O. Schweket, *Biochem. Z.* **54**, 285-90 (1913); *C.A.* **8**, 37 (1914).
26. E. W. Davy, *Chem. News.* **46**, 1 (1882).
27. E. W. Davy, *J. Chem. Soc.* **42**, 1317 (1882).
28. E. W. Davy, *Pharm. J. Trans.* [3] **13**, 466 (1883).
29. E. W. Davy, *J. Chem. Soc.* **44**, 515 (1883).

GUAIACOL

Synonym: Methylcatechol, *o*-methoxyphenol

$C_7H_8O_2$

Mol. Wt. 124.13

Beil. Ref. VI, 768.



Use: Detection of copper, hydrogen cyanide and nitrite.

Guaiacol consists of a white or slightly yellow crystalline mass, or a colorless to yellow liquid, which possesses a characteristic odor. It darkens on exposure

to air and light. The sp. gr. of the crystals is 1.129 and of the liquid 1.112. The compound solidifies at 28° C. and boils at 204-206° C. It is slightly soluble in water, soluble in glycerol, alcohol, chloroform, ether and glacial acetic acid.

Preparation: Dissolve 12 g. of o-anisidine in 27 g. of sulfuric acid (d. 1.33) and 24 ml. of water, and add 50 g. of ice. Diazotize with a chlorine-free solution of 7.5 g. of sodium nitrite in 30 ml. of water, keeping the temperature below 8° C. Dissolve 40 g. of copper sulfate, 40 g. of ammonium sulfate, 20 g. of sodium sulfate, and 60 g. of sulfuric acid (d. 1.33) in 80 ml. of water. Heat to 105° C., and into this solution pour slowly the diazo-solution. Allow to stand 1 hour and distill, and halt the distillation when the temperature reaches 105° C. Make the distillate alkaline with sodium hydroxide, and then again distill until no oil goes over. Acidify the residue with sulfuric acid, and distil the guaiacol. To purify the distillate, distill in vacuum after the addition of 0.3-0.5 per cent sodium carbonate.¹

Detection of nitrite. According to Adrian,² guaiacol yields a characteristic orange color when added to an aqueous solution of nitrous acid. Spiegel³ detects nitrous acid in water as follows:

Procedure. Shake a little of the reagent with water and filter. Mix a little of the filtrate with the water to be tested, and then acidify with a few drops of sulfuric acid. A 0.000001 N solution of nitrite gives a noticeable color.

Oxidizing agents, such as nitrates, chlorates, and hydrogen peroxide produce no color and do not interfere. Iron salts give a color with guaiacol.

Guaiacol gives an intense wine-red color when heated with a solution of a nitrite and treated with sodium hydroxide.⁴

Detection of copper and hydrogen cyanide. A guaiacol-copper sulfate mixture (10:1) gives a garnet-red color with cyanides.⁵

1. Braunlich, in Ullmann's *Enzyklopädie der technischen Chemie*, Bd. III [Berlin und Wien 1916] p. 80.

2. L. Adrian, *J. pharm. chim.* [6] 5, 174-6.

3. L. Spiegel, *Ber.* 33, 639 (1900).

4. A. Castiglioni, *Gazz. chim. ital.* 62, 1065-7 (1932); *C.A.* 27, 2678 (1933).

5. G. Gutzeit, *Helv. Chim. Acta.* 12, 713-40 (1929).

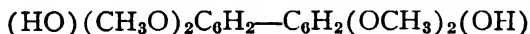
HYDROCOERULIGNONE

Synonym: 4,4'-Dihydroxy-3,5,3',5'-tetramethoxydiphenyl

$C_{16}H_{18}O_6$

Mol. Wt. 306.30

Beil. Ref. VI, 1200 (593).

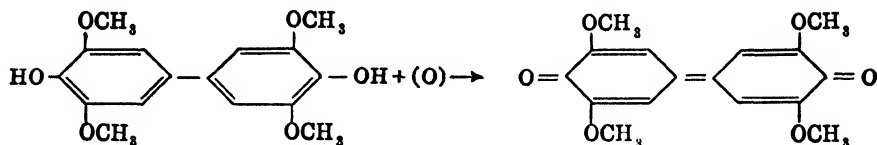
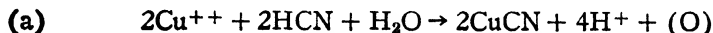


Use: Detection of hydrogen cyanide.

Hydrocoerulignone is a crystalline solid which melts at about 190° C. It is very slightly soluble in water and in ether.

Preparation: Hydrocoerulignone is prepared by reducing coerulignone by boiling with sodium bisulfite solution.¹

Detection of hydrogen cyanide. The detection of hydrogen cyanide by hydrocoerulignone is based upon the oxidizing action produced when a cupric salt is added to a solution containing cyanide. This reaction is shown in equation (a). In the presence of hydrocoerulignone the dye coerulignone is formed.



In a very dilute solution an instantaneous orange color is obtained and in a more concentrated solution a red precipitate of coerulignone is formed. The latter possesses a violet luster. This reaction is said to detect 1 part of hydrogen cyanide in 5,000,000 parts of water.^{2,3} Schar⁴ states that this reaction is less sensitive than that with guaiacol or aloin.

1. C. Liebermann and C. L. Cybulski, *Ber.* 31, 616 (1898).
2. J. Moir, *J. Chem. Met. Soc. S. Africa* 10, 342; *Chem. News* 102, 17 (1910); *C.A.* 4, 2618 (1910).
3. G. Gutzeit, *Helv. Chim. Acta* 12, 713, 829 (1929).
4. E. Schar, *Schweiz. Wochschr.* 50, 321-6, 337-41; *C.A.* 6, 2376 (1912).

4-HYDROXYBENZOTHAIOLE

$\text{C}_7\text{H}_5\text{OSN}$

Mol. Wt. 151.17

$\text{HO}-\text{C}_6\text{H}_3=(\text{SNCH})$

Use: Determination of copper, nickel and zinc.

4-Hydroxybenzothiazole is a yellow crystalline solid which melts at 143.5° C. One liter of water dissolves 0.88 g. of the reagent. Its aqueous solution is colorless but it gives a yellow solution in alcohol.

Preparation. *2-Mercapto-4-methoxybenzothiazole:* Mix 200 g. of formyl-*o*-anisidine with 170 g. of powdered sulfur and heat to boiling for 16 hours. Cool and extract the product with 2 N sodium hydroxide. Precipitate by adding hydrochloric acid, filter, and recrystallize the product from 50 per cent alcohol.

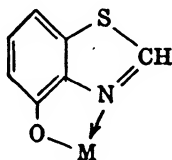
4-Methoxybenzothiazole-2-sulfonic acid: Dissolve 34 g. of the above product and 30 g. of sodium carbonate in 400 ml. of hot water and heat to 80-90° C. Slowly add with stirring 370 ml. of a 15 per cent solution of sodium hypochlorite. The completion of the oxidation may be determined by means of a drop reaction. Filter the hot mixture and mix the filtrate with a saturated solution of sodium chloride. Cool and collect the crystalline precipitate of the sodium salt of 4-methoxybenzothiazole-2-sulfonic acid.

4-Methoxybenzothiazole: Dissolve 40 g. of the sodium salt of 4-methoxybenzothiazole-2-sulfonic acid in 500 ml. of water and add to 600 g. of 5 per cent

sodium amalgam, and add with stirring the calculated quantity of 50 per cent sulfuric acid. The sulfuric acid should be added to the reaction mixture at 0° C. during the course of several hours so the acidity of the solution is sufficient to expel the sulfur dioxide. When no more sulfur dioxide is evolved, make the solution strongly alkaline and extract with warm benzene. Dry the benzene solution and concentrate strongly by evaporation. Upon cooling 4-methoxybenzothiazole separates.

4-Hydroxybenzothiazole: Heat the 4-methoxybenzothiazole with a large quantity of colorless hydrogen iodide for 1.5 hours under reflux. On cooling, the hydrogen iodide salt of 4-hydroxybenzothiazole separates in large colored crystals. Separate and dissolve the crystals in hot water. Precipitate 4-hydroxybenzothiazole from this solution with sodium bicarbonate which contains some hyposulfite. Recrystallize from dilute alcohol and purify by subliming in vacuum.¹

Determination of nickel, zinc and copper. 4-Hydroxybenzothiazole forms metallic derivatives which are somewhat similar to those obtained with 8-hydroxyquinoline. The composition of these compounds is represented by the formula:



4-Hydroxybenzothiazole forms insoluble compounds with bivalent copper, zinc and nickel, and may be used for the determination of these metals in the presence of titanium, vanadium, molybdates and tungstates.^{2,3}

4-Hydroxybenzothiazole reacts with bromine to form 4-hydroxy-5,7-dibromobenzothiazole. Thus, metallic salts of this reagent may be dissolved in dilute hydrochloric acid and titrated with potassium bromate-potassium bromide exactly as described in the section on 8-hydroxyquinoline. The following procedure may be used for the determination of nickel in the presence of titanium.

Procedure. To a solution containing about 15 mg. of nickel and 16 mg. of TiO^{++} add 1 g. of ammonium chloride and 1 ml. of 2 N ammonium hydroxide solution. Add dropwise 2.4 ml. of a 4 per cent solution of 4-hydroxybenzothiazole in methyl alcohol. Warm on a water bath for 10 minutes and carefully remove the methyl alcohol. After an hour, filter and wash the precipitate with 3 ml. of water. Dry the precipitate, wash with benzene until 4-hydroxybenzothiazole is no longer detected in the washings, and then dissolve the precipitate in 2 N hydrochloric acid. Add potassium bromide and titrate with 0.1 N potassium bromate solution as described in the section on 8-hydroxyquinoline (page 269). One ml. of 0.1 N potassium bromate is equivalent to 0.7342 mg. of nickel.

This method gives good results in the presence of 3.5 mg. of vanadate, 33.4 mg. of molybdate and 27 mg. of tungstate.

Zinc may be determined by the following procedure:

Procedure. To 20 ml. of zinc sulfate solution, containing about 15-20 mg. of zinc and 1 g. of sodium acetate, add dropwise and with stirring a 4 per cent solution of 4-hydroxybenzothiazole in methyl alcohol. Filter, wash with 10 ml. of cold water, and dissolve in warm 10 per cent hydrochloric acid. Add 0.5 g. of potassium bromide and titrate with 0.1 N potassium bromate solution. Best results are obtained by adding an excess bromide, then potassium iodide, and back titrating with sodium thiosulfate. One ml. of 0.1 N potassium bromate is equivalent to 0.8164 mg. of zinc.

Nickel may be determined by a similar procedure. Copper also can be precipitated in the same way, but good results are obtained by drying the copper precipitate at 110-20° C. and weighing as $\text{Cu}(\text{C}_7\text{H}_4\text{ONS})_2$.³ The factor for copper is 0.1730.

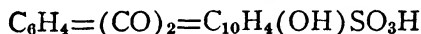
1. H. Erlenmeyer, Ueberwasser and H. M. Webber, *Helv. Chim. Acta*, **21**, 709-11 (1938).
2. H. Erlenmeyer and E. H. Schmid, *Helv. Chim. Acta*, **24**, 1159-62 (1941); *C.A.* **36**, 719 (1942).
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9-HYDROXYNAPHTHACENEQUINONE-6-SULFONIC ACID

$\text{C}_{18}\text{H}_{10}\text{O}_6\text{S}$

Mol. Wt. 354.32

Beil. Ref. XI, 353 (91).



Use: Detection of germanium.

9-Hydroxynaphthacenequinone-6-sulfonic acid consists of orange-yellow leaves. It dissolves in water to give a yellow colored solution. This turns blue-red in the presence of an alkali. 9-Hydroxynaphthacenequinone-6-sulfonic acid also dissolves in concentrated sulfuric acid to form a red solution and this is colored a yellowish-red and exhibits a yellow fluorescence with boric acid.

Preparation: Mix 50 g. of phthalic acid, 44 g. of α -naphthol and 50 g. of boric acid with 500 ml. of 97 per cent sulfuric acid and heat for an hour on an oil bath at 165° C. Pour the mixture into water and separate from the precipitate which forms. Wash the precipitate by decantation, dry, and boil with toluene. Extract the residue with boiling water, precipitate with hydrochloric acid, and treat with 10 per cent potassium hydroxide to form a difficultly soluble potassium salt. Recrystallize several times to remove any boric acid and then form 9-hydroxynaphthacenequinone-6-sulfonic acid by adding hydrochloric acid.¹

Detection of germanium. A 0.01 per cent solution of 9-hydroxynaphthacenequinone-6-sulfonic acid in concentrated sulfuric acid reacts with ger-

manium to give a bright pink color when examined in a blue light. The test is performed by evaporating a drop of the sample in a porcelain dish and adding 2-3 ml. of the reagent.²

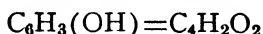
1. C. Deichler and C. Weizmann, *Ber.* **36**, 720 (1903).
2. N. S. Poluektov, *J. Applied Chem. (U.S.S.R.)*, **9**, 2302-04 (1936); *C.A.* **31**, 4615 (1937).

JUGLONE

Synonym: 5-Hydroxynaphthoquinone-1,4

$C_{10}H_6O_3$

Mol. Wt. 174.15 Beil. Ref. VIII, 308 (636).



Use: Detection of nitrite.

Juglone is a red solid which melts at 151-154° C. It is very slightly soluble in water, but is soluble in chloroform. It is moderately soluble in alcohol and ether. It is obtained as a tannin present in walnut kernels.

Detection of nitrite. If a slightly acidified nitrite solution is added to an aqueous extract of walnut kernel, a flame-red coloration is obtained. This turns violet and finally becomes blue. With a more concentrated nitrite solution, a yellow color is obtained. According to Zywnev,¹ this test applied to the detection of nitrite in water is one of the most delicate ever proposed.

1. P. Zywnev, *Z. anal. Chem.* **79**, 389-90 (1930); *C.A.* **24**, 1821 (1930).

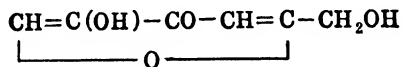
KOJIC ACID

Synonym: 5-hydroxy-2-hydroxymethyl- γ -pyrone

$C_6H_6O_4$

Mol. Wt. 142.11

Beil. Ref. XVIII, (343).

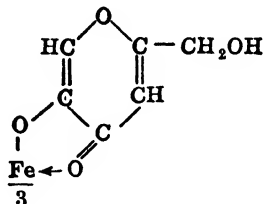


Use: Determination of iron.

Kojic acid is formed by the action of *aspergillus oryzae* on glucose sugar. It is a white crystalline solid, melting at 152° C. It is soluble in water and in alcohol, but is only slightly soluble in most other solvents.^{1,2}

Determination of iron. Corbellini and Gregorini³ and Tamiya^{4,5} have used the reaction between ferric chloride and kojic acid to determine the course of certain fermentations in which the latter compound is formed. Moss and Mellon⁶ have studied this reaction to determine its applicability to the determination of ferric iron. The reaction is of especial interest, since no organic compound previously reported for the determination of iron is a pyrone derivative. Iron and kojic acid react in a molecular ratio of 1:3 at a pH of 5-6 to yield a blue colored compound. The hydroxymethyl group is not involved in a

color reaction but instead the enolic hydroxyl group is necessary. This indicates that a possible 5-membered ring involving the carbonyl group is formed.



The intensity of the color reaction with iron depends upon the concentration of kojic acid as well as upon the concentration of the ferric ion. The concentration range over which the method is applicable depends upon the thickness of the cell and the method used for the comparison. As little as 0.05 p.p.m. of iron can be distinguished from a blank in 30 cm. Nessler tubes. Photoelectric instruments detect 0.1 p.p.m. in a 1-cm. cell. The upper limit is 20 p.p.m. The sensitivity is improved by the addition of acetone.

TABLE 33.—EFFECT OF DIVERSE IONS UPON DETERMINATION OF IRON WITH KOJIC ACID *

Ion	Added As	Permissible Concentration p.p.m.
Al ³⁺	Al(NO ₃) ₃	3
AsO ₄ ⁼	H ₂ AsO ₄	30
AsO ₆ ⁼	Na ₂ AsO ₃	170
Be ²⁺	Be(NO ₃) ₂	250
Bi ³⁺	Bi(NO ₃) ₃	25
C ₅ H ₅ O ₂ ⁼	(CH ₃ CHOHCOO) ₂ Ca	130
C ₄ H ₄ O ₅ ⁼	(NH ₄) ₂ C ₄ H ₄ O ₅	50
C ₇ H ₅ O ₅ ⁼	C ₆ H ₄ OHCOONa	500
Co ²⁺	Co(NO ₃) ₂	500
Cr ³⁺	Cr ₂ (SO ₄) ₃	10
Cr ₂ O ₇ ⁼	K ₂ Cr ₂ O ₇	5
Cu ²⁺	Cu(NO ₃) ₂	19
F ⁻	NaF	15
Hg ⁺	HgNO ₃	100
MoO ₄ ⁼	(NH ₄) ₂ MoO ₄	25
Ni ²⁺	Ni(NO ₃) ₂	330
Pb ²⁺	Pb(C ₂ H ₃ O ₂) ₂	250
PO ₄ ⁼	(NH ₄) ₂ HPO ₄	20
SiO ₃ ⁼	Na ₂ SiO ₃	100
SnCl ₄ ⁼	H ₂ SnCl ₄	10
SnCl ₆ ⁼	H ₂ SnCl ₆	5
Th ⁴⁺	Th(NO ₃) ₄	25
UO ²⁺	UO ₂ (C ₂ H ₃ O ₂) ₂	200
VO ₅ ⁼	KVO ₃	5
WO ₄ ⁼	Na ₂ WO ₄	30
Zn ²⁺	Zn(NO ₃) ₂	140
ZrO ²⁺	ZrO(NO ₃) ₂	5

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The acid concentration must be very carefully controlled within narrow limits, since it exerts a considerable influence on the hue and the color. The best pH range is between 5.5 and 7.0 during the color measurements. Ammonia may be added for adjustment of the pH only after development of the color, since otherwise some iron may be precipitated. Ammonium acetate may be used as a buffer.

Procedure. To a solution of a sample containing not more than 1 mg. of iron, add a little concentrated nitric acid and boil to oxidize the iron to the ferric state. Other oxidizing agents such as persulfate or hydrogen peroxide may be used. Dilute with iron-free water and add 1 g. of ammonium acetate. Filter if the solution is not clear, and transfer to a 100-ml. volumetric flask. Add 10 ml. of 0.1 per cent kojic acid solution, dilute to the mark and mix well. The color may be measured by any of the usual methods.

Aluminum, citrate, oxalate and pyrophosphates must be absent. A number of other ions may interfere if present in sufficiently large quantities. These are shown in Table 33, which is taken from the work of Moss and Mellon:⁶

1. T. Yabuta, *J. Chem. Soc. Japan*, **37**, 1185-1233, 1234-69 (1916); *C.A.* **17**, 1475 (1923).
2. T. Yabuta, *J. Chem. Soc.* **125**, 575 (1924).
3. A. Corbellini and B. Gregorini, *Gazz. chim. ital.* **60**, 244 (1930).
4. H. Tamiya, *Acta Phytochim. (Japan)*, **3**, 51 (1927).
5. H. N. Barham, *Ind. Eng. Chem., Anal. Ed.* **11**, 31 (1939).
6. M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.* **13**, 612-14 (1941); *C.A.* **35**, 6894 (1941).

9-METHYL-2,3,7-TRIHYDROXY-6-FLURONE

$C_{14}H_{10}O_5$

Mol. Wt. 258.22

Beil. Ref. XVIII, 176.

Use: Detection of antimony.

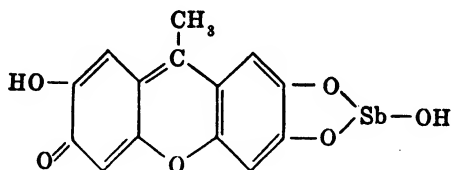
9-Methyl-2,3,7-trihydroxy-6-flurone is a moist, red powder which becomes reddish-brown when anhydrous. It does not melt, but decomposes when heated to a high temperature. It is moderately soluble in alcohol but is almost insoluble in water.

Preparation: Condense 1 mole of hydroxyhydroquinone with 1.25 moles of paraldehyde in 3-4 times the weight of ethyl alcohol containing 2 per cent sulfuric acid. Heat the mixture 1 hour on a water bath, partially evaporate to remove the alcohol and the aldehyde, and then boil rapidly with a little water. The flurone derivative is then precipitated by adding a large quantity of water. Purify by dissolving in alcohol, and again precipitate with alcohol.¹

Detection of antimony. A 0.4-0.5 per cent alcoholic solution of the reagent gives a copious red precipitate with solutions containing salts of antimony. The pH of such solutions should be 4.0. This reagent is suitable for detecting antimony on a spot plate, on filter paper, or on gelatin paper. By the spot plate technique as little as 0.2γ of antimony can be detected.²

Cerium and germanium give precipitates similar to that obtained with antimony, and iron gives a violet-black color in a buffered solution. Titanium and arsenic also give reactions with the reagent.³

The precipitate with antimony appears to be a salt in which the hydrogen of the 2,3-hydroxy groups have been replaced by SbOH. The formula assigned to this compound is



The precipitate should contain 30.8 per cent of antimony, but so far attempts to base a determination of antimony on the weight of the precipitate have proved unsuccessful.⁴

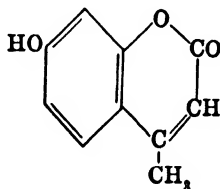
1. C. Lieberman and S. Lindenbaum, *Ber.* 37, 1177, 2731 (1904).
2. P. Wenger, R. Duckert, and C. P. Blancpain, *Mikrochim. Acta.* 3, 13-20 (1938); *C.A.* 32, 3296 (1938).
3. R. Duckert, *Helv. Chim. Acta.* 20, 362-7 (1937); *C.A.* 31, 7352 (1937).
4. P. Wenger, R. Duckert, C. P. Blancpain, *Helv. Chim. Acta.* 20, 1427-45 (1937); *C.A.* 32, 1205 (1938).

β -METHYLUMBELLIFERONE

$C_{10}H_8O_3$

Mol. Wt. 176.17

Beil. Ref. XVIII, 31.



Use: Determination of nitric acid.

β -Methylumbelliferone usually consists of colorless prisms or white needles. It melts at 185° C.

Preparation: Pour a cold solution of equal molecular quantities of resorcinol and acetoacetic ester slowly into 4-5 times as much pure concentrated sulfuric acid at such rate that there is no appreciable increase in the temperature of the mixture. Allow the mixture to stand for several hours, and then pour the reddish-yellow solution slowly onto ice. Filter, wash, and dissolve the residue in cold dilute sodium hydroxide, and again precipitate with hydrochloric acid. To purify, dry, and dissolve the solid in a little alcohol, and free from a small quantity of a reddish dye by adding a little ether. Filter and after concentration of the filtrate, recrystallize twice from alcohol.¹

Determination of nitric acid. When 2 drops of a normal nitrate solution are added to 3 drops of a .01 per cent solution of β -methylumbelliferone in concentrated sulfuric acid, nitrogen dioxide is formed, and this reacts with the reagent to form a yellow crystalline compound which is soluble in water. When the acid is neutralized with ammonia, the greenish lemon-yellow color of the solution changes to a dark straw yellow. On dilution to 2 liters with water this color changes to lemon yellow. The dilution with water is necessary since β -methylumbelliferone forms colored substances with other compounds, such as potassium chlorate which may be present along with nitrates, and these may obscure the nitrate reaction in more concentrated solutions. This reaction is sensitive to nitrous acid and nitrites also, since nitrogen dioxide may be obtained from these substances. To determine nitrates in the presence of nitrites, add a 0.1 per cent solution of the reagent in ethyl alcohol directly to a solution containing both nitrate and nitrite, and then add concentrated sulfuric acid. Under these conditions only nitrates give a positive test.

The above reactions have been used by Vasil'ev² and Vasil'ev and Dukhinova³ for the colorimetric determination of nitrates.

Procedure. Place 0.3 ml. of the sample to be analyzed in a 10 ml. pycnometer, and add 0.6 ml. of 0.1 per cent solution of β -methylumbelliferone in concentrated sulfuric acid. Prepare a series of standards containing known quantities of nitrate, and select the standard having approximately the same nitrate concentration as the unknown and treat exactly as the unknown. Place both pycnometers in a thermostat at 100° C. and leave for 3-5 minutes. Remove from the thermostat, dilute the contents somewhat with water and carefully neutralize the acid with 25 per cent ammonia until the reaction is basic. The amount of ammonia added to each pycnometer should be the same. Dilute both solutions to the mark with water and transfer to cylinders of a Dubosc colorimeter and compare in the usual manner.

The lemon yellow color which is obtained in the above procedure is quite stable and remains unchanged for several weeks. This coloration obeys the Lambert-Beer's law. This procedure requires about 15 minutes and may be used to determine nitrates in concentrations up to 0.5 γ with an accuracy of ± 1 per cent.

If the concentration of nitrate is very low, the column of liquid should be 20-30 mm. in height; and for larger concentrations 10-20 mm. By adding 0.5 ml. of a 0.03 per cent safranin solution for each 10 ml. of the solution to be analyzed, the yellow color is changed to a yellowish-pink, and this facilitates the visual evaluation of the color. The color of the safranin solution remains stable for several days.

1. H. V. Pechmann and C. Duisberg, *Ber.* **16**, 2122 (1883).
2. A. S. Vasil'ev, *J. Applied Chem. (U.S.S.R.)*, **9**, 155-6 (1936); *C.A.* **30**, 6305 (1936).
3. A. S. Vasil'ev and M. M. Dukhinova, *Zavodskaya Lab.* **10**, 35-7 (1941); *C.A.* **35**, 5061 (1941).

PENTACHLOROPHENOL C_6HOCl_5

Mol. Wt. 266.36

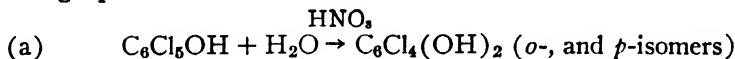
Beil. Ref. VI, 194.

 $C_6Cl_5(OH)$ **Use:** Detection and determination of nitrate.

Pentachlorophenol is a crystalline solid melting at 190-191° C. It is easily soluble in alcohol and ether and is moderately soluble in benzene. It is only very slightly soluble in cold ligroin.

Preparation: Pass chlorine into 1000 g. of phenol until the increase in weight corresponds to the formation of trichlorophenol. Then add 30-40 g. of dry ferric chloride and again add chlorine with gradual heating on an oil bath at a temperature of 130-40° C. until the increase in weight indicates the conversion of the phenol to the pentachloro derivative. Treat the cold mass with twice as much petroleum ether. Separate the petroleum ether from the residue and remove any adhering petroleum ether by evaporation. Take up the residue in warm sodium hydroxide solution, remove colored impurities by adding a weight of sodium peroxide corresponding to 2-3 per cent of the weight of pentachlorophenol. Filter and precipitate by adding a slight excess of hydrochloric acid. Filter, wash with cold water, and finally purify by crystallizing from benzene.¹

Detection and determination of nitric acid and nitrates. Pentachlorophenol is easily converted into chloranil (tetrachloroquinone) according to the following equations:



Both ortho and para quinones are formed.

This reaction may be used for the detection and determination of nitric acid and nitrates. The following method is used to detect nitrates:²

Reagent. Dissolve 10 g. of pentachlorophenol in 500 ml. of glacial acetic acid and add 100 ml. of concentrated sulfuric acid.

Procedure. Acidify the solution to be tested with acetic acid and evaporate to dryness. Repeat this operation several times to eliminate nitrites. Dissolve the residue in a little water and treat with 2 or 3 drops of the reagent. A yellow or yellowish-red color appears if nitrates are present.

This reaction may be carried out as a spot test as follows:

Procedure. Acidify a few drops of the solution to be analyzed with acetic acid and evaporate to dryness as described above. To the residue add a drop of a 10 per cent aqueous solution of sodium salt of pentachlorophenol. Then add 2 or 3 drops of concentrated sulfuric acid. A yellow or yellowish-red color appears with nitrates.

The color obtained with nitrates and pentachlorophenol is suitable for the colorimetric determination of small quantities of nitrate or nitric acid:

Procedure. According to the concentration of the solution, evaporate 10 ml. or more to dryness after acidifying with acetic acid. Repeat this operation 2 or 3 times. If the solution to be analyzed is strongly acid with mineral acid, neutralize with sodium hydroxide, acidify with acetic acid, and proceed as described above.

Dissolve the residue in the least possible quantity of water and add 10-20 ml. of the solution of pentachlorophenol in acetic and sulfuric acids (see above).

Heat on a water bath for half an hour. If a turbidity results, add more of the pentachlorophenol reagent. Compare the resulting color with a standard solution of potassium nitrate which has been similarly treated. Results claimed for this method are accurate to 0.05 mg. of potassium nitrate.

A similar method has been used for the determination of oxides of nitrogen in air.³ The reaction between pentachlorophenol and nitric acid has also been studied in connection with a method for the determination of pentachlorophenol in tissues and water.⁴

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PYROGALLOL DIMETHYLETHER

Synonym: 1-Hydroxy-2,6-dimethoxybenzene

$C_8H_{10}O_3$

Mol. Wt. 154.16

Biel. Ref. VI, 1081



Use: Detection of chromic acid, ferric salts, and nitrous acid.

Pyrogallol dimethylether is a white crystalline solid. It melts at 55-56° C., and boils at 260-263° C. It is soluble in about 50 parts of water and in alcohol.

Preparation: Dissolve 1 mole of pyrogallol, 2 moles of potassium hydroxide, and 2 moles of methyl iodide in absolute methyl alcohol and heat to 150-160° C. for 4-5 hours. Evaporate the alcohol on a water bath and mix the residue with mineral acid. Dissolve the oil in sodium hydroxide and evaporate the dark solution several times almost to dryness on a water bath. Acidify the residue, extract with ether and crystallize.¹

Reaction with chromic acid, ferric salts and nitrous acid. A solution of potassium dichromate which has been acidified with sulfuric acid yields a yellow-red color when treated with a few drops of a 2 per cent aqueous solution of pyrogallol dimethylether. As little as 0.02 mg. of potassium dichromate in 10 ml. can be detected by this reaction. In more dilute solutions the color is shaken

out with chloroform, which is colored yellow. In this way 0.001-0.002 mg. of CrO_3 can be detected. The hydrogen peroxide reaction for chromates is not applicable to quantities of CrO_3 less than 0.04 mg.^{2,3}

Ferric chloride reacts with the reagent to give a yellow-red color. A yellow coloration is also obtained with solutions containing as little as 0.008 mg. of potassium nitrite in 5 ml. Very dilute solutions of chlorine and bromine also give yellow colorations. The reagent used in these tests must be freshly prepared since it becomes yellow on standing.

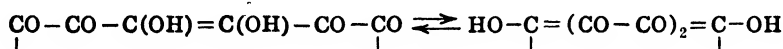
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RHODIZONIC ACID

$\text{C}_6\text{H}_2\text{O}_6$

Mol. Wt. 170.08

Beil. Ref. VIII, 535.



Use: Detection of barium, lead, strontium, sulfate and tin.

Sodium rhodizonate and not the free acid is used as the analytical reagent. The sodium salt is a violet crystalline solid which dissolves in water to yield an orange-yellow solution. It is slightly soluble in a solution of sodium carbonate, but is insoluble in alcohol.

Rhodizonic acid can be used only in the form of its alkali salt. The orange to yellow color of its aqueous solution slowly changes and finally disappears due to the slow oxidation of rhodizonic acid to croconic acid and leuconic acid.^{1,2} The decomposition of sodium rhodizonate is accelerated by ultraviolet light, particularly if the salt is finely divided in the capillaries of paper.

Preparation: Place 220 g. of hydroquinone in a large evaporating dish and add 408 g. of acetic anhydride and 2 ml. of concentrated sulfuric acid. Warm the mixture slightly until the solid is dissolved. Then cool the dish in ice. Triturate the crystalline mass which forms with an excess of ice water, filter with suction and wash with about 2 liters of cold water. The product is diacetylhydroquinone.

Add the diacetylhydroquinone in small quantities to 6 parts of fuming nitric acid ($d = 1.5$) contained in a flask immersed in ice. Stir during this operation. Cool with a 2:1 snow-salt mixture and add approximately 3 per cent of ammonium chloride. The temperature of the mixture ought to be at approximately -25°C . Cool 6 parts of concentrated sulfuric acid to -15°C . and allow to flow dropwise into the solution with continual agitation. The temperature ought not exceed -6°C . When all the sulfuric acid has been added a yellow semi-fluid mass is obtained. Continue to stir for 30 minutes and allow to stand for 3 hours at -3°C . until a small part of the crystalline mass gives a greenish-brown and not a violet color when dissolved in ice water and made alkaline with potassium hydroxide. Pour the mixture on about 15 parts of crushed ice with continual agitation. The temperature should never rise above 0°C . Nitranilic acid sepa-

rates in the form of yellow crystals. Filter rapidly with suction while cooling with a piece of ice. The pasty residue is immediately mixed with crushed ice. Mix with stirring with a solution of potassium hydroxide cooled to -5°C . and let stand for 12 hours and recrystallize the yellow potassium nitranilate.

Treat the potassium salt in a large porcelain dish with a solution of 3 parts of stannous chloride dissolved in 20 parts of a mixture of equal parts of water and hydrochloric acid. A brown solution is formed which immediately solidifies to a brownish-violet crystalline solid. Add immediately a large quantity of granulated zinc. The solution becomes colorless and tin is precipitated. Heat a little on a water bath if necessary. When the solution no longer contains tin, press the spongy metal into a small mass and decant the warm liquid through glass wool. Pass through the solution a stream of hydrogen chloride gas to precipitate the hydrochloride of diaminotetrahydroxybenzene. Redissolve the gray crystals in the least possible quantity of boiling water and recrystallize by the addition of concentrated hydrochloric acid.

Add the diaminotetrahydroxybenzene hydrochloride, in small portions, to three parts of concentrated nitric acid cooled in crushed ice and very little salt. Agitate the mixture continually. In a short time the liquid begins to crystallize. Then dilute with an equal volume of water. The temperature should not exceed 30°C . Allow the reaction mixture to stand and add a 1:1 mixture of ether and alcohol. Filter the precipitate of triquinolyl and wash first with ice water and then with the ether-alcohol mixture.

Mix 20 g. of the triquinolyl with 32 ml. of a saturated solution of sodium chloride at 45°C . Shake the mixture to dissolve the triquinolyl. The impurities remain undissolved. Filter immediately on a porcelain funnel heated to 40°C . and cool the yellow filtrate in a salt-ice mixture. The triquinolyl is crystallized by rubbing the walls of the flask with a glass rod. Filter with suction and wash first with alcohol and then with ether.

Sodium rhodizonate is prepared by reducing triquinolyl with a saturated solution of sulfurous acid and heating to 50°C . The yellow liquid which is formed is saturated with sodium carbonate, and by this treatment violet crystals are obtained. Wash with very little ice water and then with absolute alcohol.^{3,4}

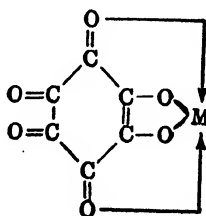
Detection of barium and strontium. Sodium rhodizonate yields colored precipitates when added to solutions of barium and strontium salts. Feigl⁵⁻⁸ first used this reaction for the detection of barium and strontium. The formation and decomposition of barium rhodizonate have also made possible the use of sodium rhodizonate as an indicator in the volumetric determination of barium and sulfate.^{9,10,11,19,20,21}

Sodium rhodizonate reacts with certain univalent and divalent cations to produce colored precipitates, but no visible reaction is obtained with trivalent or tetravalent cations. Bismuth is an exception, probably because of the occurrence of the bismuthyl radical, BiO^+ . Feigl and Suter² have studied the reactions of neutral and acid 1 per cent solutions of various metallic salts with sodium rhodizonate. They have also observed reactions of sodium rhodizonate with the corresponding oxides and hydroxides. The results of this study are shown in Table 34.

TABLE 34.—REACTIONS WITH SODIUM RHODIZONATE

Metal Ion	Metal Salt Solution		Hydroxide	Oxide
	Neutral	pH—2.8		
Ag ⁺	Black	Black
Hg ⁺	Brown-red	Brown-red (disappears on standing)
Tl ⁺	Dark-brown	Dark-brown
Pb ⁺⁺	Blue-violet	Scarlet	Blue-violet	Blue-violet
Cu ⁺⁺	Orange-red
Hg ⁺⁺	Red-orange
Cd ⁺⁺	Brown-red	Brown-red	Gray-brown
Bi ⁺⁺⁺	Brown-red	Brown-red
Ni ⁺⁺
Co ⁺⁺
Zn ⁺⁺	Brown-violet	Brown-violet	Brown-violet
Mn ⁺⁺
UO ₂ ⁺⁺	Brown
Be ⁺⁺
Mg ⁺⁺
Ca ⁺⁺	Brown-red	Brown-red
Ba ⁺⁺	Red-brown	Red-brown	Red-brown	Red-brown
Sr ⁺⁺	Red-brown	Red-brown	Red-brown
Sn ⁺⁺	Violet	Violet
Sn ⁺⁺⁺⁺
Al ⁺⁺⁺
Zr ⁺⁺⁺⁺

Ferrous salts in neutral solution yield a red-brown precipitate, which rapidly turns to a bluish-black, probably due to oxidation. In solutions of pH 2.8 there is no reaction. Ferric salts yield no precipitate but cause a blue-green color. This apparently is due to the fact that sodium rhodizonate is a phenol, and therefore reacts with ferric salts like other phenols. In the presence of fluoride, no color reaction is obtained. The color of the water-soluble rhodizonates and of the soluble alkaline salts is caused by the formation of inner-complex salts. The two acid hydrogen atoms are located adjacent to carbonyl groups, which are capable of developing auxiliary valences and forming 5-membered rings.



Feigl⁸ recommends the following method for detecting barium by a spot test.

Procedure. Place a drop of neutral or slightly acid solution to be tested on a strip of filter paper and add a drop of a 5 per cent aqueous solution of sodium rhodizonate. A reddish-brown to brown spot appears depending upon the amount of barium present. This method will detect 0.25 γ of barium at a concentration of 1:200,000.

Strontium and barium react similarly with sodium rhodizonate, but strontium rhodizonate is soluble in cold dilute hydrochloric acid, while the barium compound is converted into an insoluble acid salt, which has a bright red color similar to that of nickel dimethylglyoxime. In a test tube reaction, small quantities of barium rhodizonate appear to dissolve when treated with hydrochloric acid, but this is due to the conversion of the red barium salt to a very finely divided form which is difficult to see. If, however, the reaction is carried out on filter paper, the reddish-brown stain of barium rhodizonate is converted by 1:20 hydrochloric acid into a bright red color. If no brown stain is obtained on treating a drop of the test solution with a drop of sodium rhodizonate on filter paper, the absence of both barium and strontium is indicated, while a brown stain may indicate the presence of either or both metals. If the stain disappears with dilute hydrochloric acid, strontium only is indicated, but if the stain turns red, barium or both barium and strontium are present. By this method, 0.5 γ of barium can be detected in the presence of more than 50 times as much strontium.

Barium carbonate is more soluble than calcium or strontium carbonate; hence, if the precipitate obtained by treating strontium and barium salts with ammonium carbonate is thoroughly washed and treated with sodium rhodizonate, a red-brown color appears with barium. Calcium and strontium carbonates do not react under these conditions.²

Mutschin and Pollak¹² claim that as little as 2.5 mg. of barium in 250 ml. of solution can be detected by placing a drop of test solution on a strip of filter paper freshly impregnated with sodium rhodizonate. Ammonium, sodium, potassium, lithium, and calcium salts do not interfere.

Although strontium salts, like barium salts, react with sodium rhodizonate to give a red-brown precipitate, strontium can be detected in the presence of barium. By treating a mixture of barium and strontium salts with potassium chromate, barium is converted to the insoluble chromate, which does not react with sodium rhodizonate. The more soluble strontium salt gives the characteristic test.

Procedure. Place a drop of the solution to be tested on filter paper that has been impregnated with a saturated solution of potassium chromate and allowed to dry. Allow to stand for 1 minute and treat the spot with a drop of 5 per cent solution of sodium rhodizonate. A reddish-brown spot indicates strontium. This test is sensitive to 3.9 γ of strontium in the presence of 84 times as much barium.

If barium is known to be absent the test for strontium may be applied as described for barium and is capable of detecting 0.45% of strontium. Davies¹³ has used sodium rhodizonate to detect strontium in a scheme of analysis.

Detection of sulfate. Barium rhodizonate is stable toward acetic acid and dilute hydrochloric acid, but is decomposed by the sulfate ion. This behavior of the barium salt has been used by Gutzeit^{4,14} for the detection of sulfate.

Procedure. Place a drop of barium chloride solution on filter paper and treat with a drop of freshly prepared sodium rhodizonate solution. Add to the red spot a drop of acid or alkaline solution to be tested. The red spot disappears if sulfate is present.

Detection of lead. Lead salts react with sodium rhodizonate in a neutral solution to yield a blue-violet amorphous precipitate of $\text{PbC}_6\text{O}_6 \cdot \text{Pb}(\text{OH})_2 \cdot \text{H}_2\text{O}$. In a solution of pH 2.8 a crystalline scarlet-red precipitate of $2\text{PbC}_6\text{O}_6 \cdot \text{Pb}(\text{OH})_2 \cdot \text{H}_2\text{O}$ is obtained. Under well-defined conditions the formation of the lead salts can be used as a sensitive test for lead.^{1,2,15,16,17,22,23} The formation of either the blue-violet or the scarlet-red compound can be used to detect lead. It is best in testing in neutral solutions which contain no interfering ions to regulate conditions such that the blue-violet salt is formed. The test for lead may be carried out as follows:²

Procedure. Place a drop of solution to be tested on filter paper and treat the spot with a drop of 0.2 per cent sodium rhodizonate solution. A blue-violet color indicates the presence of lead. This test will detect 0.1% of lead at a concentration of 1:500,000.

Thallium, silver, cadmium, barium and stannous tin also react at a pH of 2.8. In the presence of such interfering substances it is best to separate lead as the chloride, along with silver, mercurous mercury and thallous thallium, according to the usual scheme of qualitative analysis:

Procedure. Precipitate the chlorides with hydrochloric acid and without washing transfer to a crucible. Dry by gentle warming, and then carefully heat to redness to volatilize thallous and mercurous chlorides. Treat the cold residue with 4 drops of concentrated ammonium hydroxide to dissolve silver, and evaporate the contents of the crucible to dryness. Add 3 drops of buffer solution prepared by dissolving 15 g. of tartaric acid and 19 g. of sodium bitartrate in a liter of solution, and then add 1 drop of sodium rhodizonate solution. A red precipitate or coloration appears if lead is present.

By this procedure lead may be detected in the presence of all other metals, and the test is more sensitive than tests based on dissolving the lead chloride in hot water and treating with various reagents.

Detection of tin. Tin may be detected by the violet color which forms when stannous tin in a solution of pH 2.8 is treated with a solution of sodium rhodizonate.^{2,18}

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SALICYLIMINE

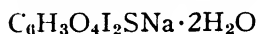
Use: Detection of copper and nickel.

Determination of copper and nickel.

Salicylaldehyde reacts with ammonia in an aqueous solution to form salicylimine, $C_6H_4(OH)CH=NH$. This compound forms chelate compounds with a number of metals, including copper and nickel, through replacement of the phenolic hydrogen atom and coordination of the metal with the imine nitrogen atom. This reaction has been used for the detection and determination of copper and nickel.¹ For the details of this procedure, see section on salicylaldehyde.

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SOZOIODOL Synonym: Sodium salt of 2,6-diiodophenol-4-sulfonic acid



Mol. Wt. 484.01

Beil. Ref. XI, 245.



Use: Detection of lead, mercury, nitrite, silver and thallium.

The free acid crystallizes from water as the trihydrate. It becomes anhydrous at 100° C. and melts at 120° C. It is readily soluble in water.

Preparation: 2,6-diiodophenol-4-sulfonic acid is obtained by treating an excess of the potassium salt of *p*-phenolsulfonic acid in dilute hydrochloric or sulfuric acid with 1 molecular weight of iodine in the form of a solution containing the calculated quantity of potassium iodide and potassium iodate.^{1,2}

Detection of nitrite. Castiglioni^{3,4} observed that sozoiodol yields a color reaction with small quantities of nitrite. The test is performed as follows:

Procedure. Add several mg. of sozoiodol to 1 ml. of a solution containing nitrite and heat to boiling. The phenolic group yields sufficient hydrogen ion to convert the nitrite to nitrous acid, and this in turn reacts to form a nitroso derivative of the reagent. This causes an intense cherry-red color after heating. An orange-yellow color is obtained in a solution containing 1 part of sodium nitrite in 100,000 parts of water.

Detection of lead, silver, mercury and thallium. A concentrated aqueous solution of sozoiodol forms crystalline precipitates with silver, lead, mercurous and thallous salts. These are easily distinguished from one another under a microscope.⁵

Lobo⁶ recommends the following test for mercury.

Procedure. Add a drop of 2 per cent solution of sozoiodol to a drop of solution to be tested. In the presence of 5% or more of mercurous mercury, rosettes of bright yellow needle-like crystals form. The precipitate is insoluble in dilute sulfuric or nitric acid.

Under the same conditions lead may form a pale yellow precipitate, but precipitates obtained with other cations are white.

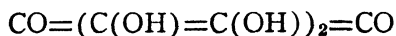
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TETRAHYDROXYQUINONE Synonym: Tetrahydroxybenzoquinone

$C_6H_4O_6$

Mol. Wt. 140.09

Beil. Ref. VIII, 534.



Use: Detection and determination of barium, indicator in the titration of sulfate with barium.

Tetrahydroxyquinone is a blue-black crystalline solid which appears yellow in transmitted light. It is slightly soluble in cold water, but is freely soluble in hot water and in alcohol. It is only slightly soluble in ether. The compound reacts as a strongly dibasic acid. Its sodium salt ($Na_2C_6H_2O_6$) is an almost black, crystalline solid, which is only sparingly soluble in water.

Preparation: Prepare a hot saturated solution of hexahydroxybenzene, cool, and mix with sodium carbonate. The surface of the mixture turns dark yellow,

and a green crystalline solid separates. The formation of this compound is accelerated by passing a stream of air through the mixture. Filter, and wash free of sodium carbonate with water. The almost black, insoluble compound is the sodium salt of the reagent. To obtain the free acid, boil the sodium salt with dilute hydrochloric acid. Tetrahydroxyquinone separates as blue-black crystals on cooling.^{1,2}

Detection of barium. Tetrahydroxyquinone has been used for the detection of barium. It forms with barium salts a red to pink color or a precipitate which is insoluble in dilute hydrochloric acid. A hot saturated solution of the quinone is used as the reagent.^{3,4} This reaction does not constitute a particularly sensitive test for barium, but it is, nevertheless, a rather important one, since few reagents give color reactions with any of the alkaline earths.

Lead gives a red precipitate, soluble in dilute acids, and strontium gives a light brown precipitate which is soluble in dilute hydrochloric acid.

Determination of sulfate. Tetrahydroxyquinone has been used as an indicator for the titration of sulfates with solutions of barium chloride.⁵⁻⁹ It is similar to rhodizonic acid.

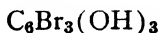
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TRIBROMOPYROGALLOL



Mol. Wt. 362.83

Beil. Ref. VI, 1085 (540).



Use: Detection of bismuth.

Tribromopyrogallol is a crystalline solid. It is soluble in hot water.

Preparation: Tribromopyrogallol is prepared by rubbing together pyrogallol and bromine.¹

Detection of bismuth. A nitric acid solution of tribromopyrogallol gives an orange-yellow precipitate with solutions of bismuth salts. A yellow zone is obtained by shaking with ether. This reaction is sensitive to 8γ of bismuth per ml.²

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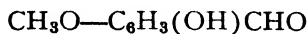
VANILLIN

Synonym: 4-Hydroxy-3-methoxybenzaldehyde, methylprotocatechuic aldehyde

$C_8H_8O_3$

Mol. Wt. 152.14

Beil. Ref. VIII, 247.



Use: Detection of chlorine and iron.

Vanillin consists of white or slightly yellow crystalline needles. It has a rather pleasant aromatic odor and tastes of vanilla. It oxidizes slowly on exposure to moist air. It melts at 80-81° C. and boils at 285° C. One gram of the solid dissolves in 100 ml. of water, but it is freely soluble in alcohol, chloroform, ether and carbon disulfide and glacial acetic acid.

Detection of iron. An aqueous solution of vanillin reacts with ferric chloride to yield an intense but clear blue-violet color. This reaction may be used for the detection of ferric salts.^{1,2}

Detection of chlorine. Raikow³ has used vanillin in a reagent for the detection of chlorine in benzoic acid.

Reagent. Dissolve 1 g. of vanillin and 1 g. of phloroglucinol in 100 ml. of ether.

Procedure. Place 0.5 ml. of the reagent in a porcelain crucible lid and allow the mixture to stand until the ether has evaporated. Then hold the inverted lid and the residue over the flame of an alcohol lamp in which the benzoic acid to be tested is ignited on a platinum loop. The residue on the lid becomes rose-red to carmine-red depending on the quantity of chlorine present in the acid.

Detection of hydrochloric acid. Günzburg⁴ and others^{5,6,7} have used vanillin in a reagent for the detection of hydrochloric acid in gastric juice.

Reagent. Dissolve 2 g. of phloroglucinol and 1 g. of vanillin in 40 ml. of alcohol.

Procedure. Evaporate equal volumes of gastric juice and reagent in an evaporating dish. A red residue remains if free hydrochloric acid is present. The sensitiveness of this reaction is 1:10,000 to 1:20,000.

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CHAPTER XI

AMINO PHENOLS

Phenols having an amine group in the ortho or para position are easily oxidized by inorganic oxidizing agents, and may be used in analytical procedures for the detection and determination of these substances. Amino phenols and amino naphthols have been used in the molybdenum blue reaction for the reduction of silicomolybdic and phosphomolybdic acids in procedures for the colorimetric determination of silicon and phosphorus, and for the indirect determination of calcium after precipitation as calcium phosphate. Silver and copper may be determined after reduction to the metal by amino phenols, and various oxidizing agents give color reactions by the oxidation of these substances. Other analytical reactions of the amino phenols are based on the formation of chelate rings through replacement of the phenolic hydrogen atom by a metal, and coordination of the metal atom with the amino nitrogen atom.

1-AMINO-8-NAPHTHOL-4,6-DISULFONIC ACID Synonym: K acid

$C_{10}H_9O_7NS_2$

Mol. Wt. 319.30

Beil. Ref. XIV, 839.

$(HO_3S)_2C_{10}H_4(NH_2)OH$

Use: Detection of chlorate, nitrate, nitrite and other oxidizing agents.

Preparation: Heat 200 g. of 1-naphthylamine-4,6,8-trisulfonic acid (sodium salt) with 300 g. of sodium hydroxide and 120 ml. of water in an autoclave at 170° C. until a test shows no further increase of the blue fluorescence of the dye in an alkali or acetic acid solution. Cool and acidify the melt with hydrochloric acid. The dye separates as the acid sodium salt.¹

The reagent may also be prepared by converting naphthalene to the 1,5-disulfonic acid and then further sulfonating to the 1,3,5-trisulfonic acid. While still in the sulfonation mixture, dilute with ice and cool, and then nitrate the cold mixture with the theoretical quantity of mixed acid. Reduce with iron and fuse with sodium hydroxide in an autoclave to obtain 1-amino-8-naphthol-4,6-disulfonic acid.

Detection of nitrite. In the presence of nitrous acid, sulfanilic acid is converted to a diazo compound which, upon coupling with 1-amino-8-naphthol-4,6-disulfonic acid, yields a brilliant, Bordeaux-red color which may be used as an extremely sensitive test for nitrite. This reaction was suggested by Erdmann,² who performs the test in the following manner:

Procedure. Mix 50 ml. of the solution to be tested with 5 ml. of an acidified solution containing 2 g. of sodium sulfanilate per liter, and then add

about 0.5 g. of 1-amino-8-naphthol-4,6-disulfonic acid. In the presence of nitrite, a brilliant, Bordeaux-red color appears. This color reaches its maximum intensity in about 1 hour.

This test is strongly recommended by Mennicke,^{3,4} who states that the reaction is sensitive to 1 part of nitrite in 300,000,000 parts of solution. Nitrate does not interfere. Romijn,⁵ who has studied various nitrite tests, states that Erdmann's method is less satisfactory than others based upon the same principle.

Vagi⁶ has used a test similar to that proposed by Erdmann,² but in which benzidine is substituted for sulfanilic acid:

Procedure. The reagent is prepared by dissolving 1 g. of benzidine and 1 g. of 1-amino-8-naphthol-4,6-disulfonic acid in 100 ml. of 80 per cent acetic acid and diluting with 300 ml. of water. To make the test, add 5 ml. of reagent to 40 ml. of solution to be tested. A red color is obtained with nitrite.

Detection of nitric acid and other oxidizing agents. Vagi⁷ has used 1-amino-8-naphthol-4,6-disulfonic acid for the detection of nitric acid, ferric chloride, chlorate, nitrous acid and other oxidizing agents. The test for nitrate is carried out as follows:

Procedure. Mix 5 ml. of the solution to be tested with 5 ml. of concentrated sulfuric acid and add 1 drop of an aqueous solution of 1-amino-8-naphthol-4,6-disulfonic acid. A red or orange color appears in the presence of as little as 15 mg. of potassium nitrate per ml. of solution.

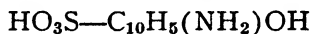
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1-AMINO-2-NAPHTHOL-4-SULFONIC ACID

$C_{10}H_9O_4NS$

Mol. Wt. 239.25

Beil. Ref. XIV, 846.



Use: Determination of calcium, phosphorus and silicon.

1-Amino-2-naphthol-4-sulfonic acid is a white crystalline solid. It is insoluble in water, alcohol, ether and benzene. It is soluble in alkalis and in solutions of sodium bisulfite.

Preparation: Convert 300 g. of β -naphthol into α -nitroso- β -naphthol (see section on α -nitroso- β -naphthol), and transfer the product to a 6-liter vessel. Use a cold solution of 600 g. sodium bisulfite and 100 ml. of 6 N sodium hydroxide in 2 liters of water to transfer the material. Dilute to 4-4.5 liters and stir the mix-

ture until solution is complete. Filter with suction and dilute the clear yellowish-brown filtrate to 7 liters with water. Stir vigorously and slowly add 400 ml. of concentrated sulfuric acid by pouring down the side of the vessel. Place the mixture in a hood and protect from light. Allow to stand 4-5 hours and filter. Place the residue in a 1-liter beaker and wash with 200 ml. of water. Filter, wash the residue with 300 ml. of water on the filter. Dry to constant weight at 120° C.

The commercial product may require purification before use. A method described by Folin ¹ may be used for this purpose:

Purification. Heat 1 liter of water to 90° C. and dissolve in it 150 g. of sodium bisulfite and 10 g. of crystalline sodium sulfite. Then add to this mixture 15 g. of the crude 1-amino-2-naphthol-4-sulfonic acid and shake until all but an amorphous impurity is dissolved. Filter the hot solution through a large paper, cool the filtrate in running water, and pour into 10 ml. of concentrated hydrochloric acid. Filter with suction, and wash the precipitate, first with 300 ml. of water and finally with alcohol until the washings are colorless. Dry in air with the least possible exposure to light and store in a brown bottle.

Determination of phosphorus. Small quantities of phosphorus are usually determined colorimetrically by reducing the phosphomolybdate, formed in the reaction of a phosphate with ammonium molybdate, to a blue colored compound. Various reducing agents have been employed for this purpose. The most common of these are: hydrazine sulfate, stannous chloride, hydroquinone, benzidine and 1-amino-2-naphthol-4-sulfonic acid. Fiske and Subbarow ² have used 1-amino-2-naphthol-4-sulfonic acid for the reduction of phosphomolybdic acid rather than hydroquinone, which has been recommended by Bell and Doisy ³ (page 124) and Briggs ^{4,5} (page 124). The reduction with 1-amino-2-naphthol-4-sulfonic acid is complete in about 5 minutes and the color is permanent, and most of the substances likely to be present in the analysis of biological materials do not interfere unless present in excessive amounts. With the use of hydroquinone, about 30 minutes are required for the color to develop, and there is a lack of proportionality of the color produced with solutions of different strengths. Further, 1-amino-2-naphthol-4-sulfonic acid is said to be less affected by ammonium and ferric salts, nitrites, nitrates, chlorides, and silicates, all of which interfere with the color development with hydroquinone.^{2,6}

Vasarehelyi ⁷ has studied the various isomeric aminonaphtholsulfonic acids and reports that the 1,2,4-compound is the most satisfactory. Kuttner and Cohen ⁸ have found the 1,4,6-compound to be equally effective.

The following method is recommended by the American Public Health Association ⁹ for the determination of small quantities of phosphate in water:

Reagents. *Sodium bisulfite solution:* Dissolve 150 g. of sodium bisulfite, $\text{Na}_2\text{S}_2\text{O}_5$, in 1 liter of distilled water.

Sodium sulfite solution: Dissolve 20 g. of sodium sulfite, Na_2SO_3 , in 100 ml. of distilled water.

1-Amino-2-naphthol-4-sulfonic acid reagent: Grind 0.5 g. of 1-amino-2-naphthol-4-sulfonic acid and mix with 5 ml. of the sodium sulfite solution and

then dissolve in 195 ml. of sodium bisulfite solution. The quantity of sodium sulfite used should not be greater than that required to dissolve all 1-amino-2-naphthol-4-sulfonic acid, since its presence causes the resulting solution to be less stable. The solution may be heated if necessary to 50-60° C. to hasten solution. The reagent should be stored in a dark well-stoppered bottle and should be prepared fresh every 2 weeks. The purified grade reagent must be used since the technical product does not give satisfactory results.

Ammonium molybdate solution: Dissolve 25 g. of ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in 200 ml. of distilled water. Transfer this solution to a 1-liter flask containing 500 ml. of 10 N sulfuric acid, and dilute to the mark with distilled water.

Standard phosphate solution: Dissolve 0.2865 g. of thoroughly dried pure monopotassium phosphate, KH_2PO_4 , in a little distilled water, and dilute to 1 liter with distilled water.

Procedure. Pour exactly 50 ml. of the filtered sample containing less than 40 p.p.m. of phosphate into a 100-ml. graduated cylinder. If 50 ml. of the sample contains more than 40 p.p.m. of phosphate, use a 25-ml. sample and multiply the final result by 2. Next add 1 drop of phenolphthalein and then 10 N sulfuric acid until the solution is colorless. This step may be omitted if the sample contains less than 500 p.p.m. of hydroxide and no silica. If the sample contains silica, or if it is not known whether silica is present or not, add exactly 1 additional ml. of 10 N sulfuric acid.

Place exactly 3 ml. of the standard phosphate solution in a second 100-ml. graduated cylinder and dilute both solutions to about 70 ml. Shake well and add exactly 10 ml. of the ammonium molybdate solution from a pipet. Again shake, and add exactly 4 ml. of the 1-amino-2-naphthol-4-sulfonic acid reagent and dilute both solutions to 100 ml. Allow the mixtures to stand for 5 minutes, and pour 50 ml. of the standard solution into a Nessler tube. Pour the unknown solution into a second tube until upon looking down through the tubes the colors appear to match. From the graduation on the tube, determine the volume of unknown required to match the color of the standard. Pour the unknown from the Nessler tube back into the graduate and see that the volume is exactly 100 ml. Make 3 readings in the manner described above and calculate the phosphate concentration as follows:

$$\frac{600}{\text{ml. of unknown}} = \text{p.p.m. phosphate}$$

The average of the 3 readings is taken as p.p.m. of phosphate in the original sample. If the solution is high in phosphate, the volume of the unknown should be read to the nearest 0.5 ml.

If the temperature of the standard solution does not exceed 20° C. appreciably, it will be stable for 1 hour. By preparing unknowns in sets of 4 or 5 it is possible to compare 15 or 20 unknowns with 1 standard.

1-Amino-2-naphthol-4-sulfonic acid has been used for the colorimetric determination of phosphorus in blood;^{10,11,12} in urine;¹² in plant materials;²⁶ muscle

extract;¹⁴ and in grass¹⁵ and other biological materials.^{14,16-19} Organic acids, such as lactic, maleic, pyruvic, glycolic, citric, oxalic, tartaric and glycerophosphoric interfere.¹⁷

The following procedure by Lohmann and Jendrassik¹⁴ may be used for the colorimetric determination of phosphate in muscle extract:

Reagent. The reagents used are the same as those described above.

Procedure. Deproteinize 1 ml. of muscle extract containing 0.1-1.0 mg. of P_2O_5 with 4-6 ml. of 7 per cent trichloroacetic acid and filter. Transfer a suitable aliquot of the filtrate to a 25-ml. flask and treat with 5 ml. of the ammonium molybdate reagent and 1 ml. of the 1-amino-2-naphthol-4-sulfonic acid solution. Simultaneously prepare 1 or 2 standards, using the standard phosphate solution and treating exactly like the unknown. An equivalent quantity of trichloroacetic acid is added to each standard. Dilute both standards and unknown to the 25-ml. mark, and allow to stand for 5 minutes at 37° C. Examine colorimetrically by the usual method. The temperature should not differ more than 1-2° C. during the examination. Best results are obtained with solutions containing 0.2-0.4 mg. of P_2O_5 .

The colorimetric method of Lohmann and Jendrassik¹⁴ may be slightly modified to determine orthophosphate in the presence of meta- and pyrophosphates.²⁰ Instead of heating to 37° C., Boratynski²⁰ recommends heating for 10 minutes at 25° C. and then allowing to cool for 5 minutes before comparison. The color reaction is not given by meta- or pyrophosphates, but when much of the latter is present, a larger quantity of molybdate is necessary.

Determination of calcium. Small quantities of calcium may be determined by precipitating as calcium phosphate and then determining the calcium indirectly by estimating the phosphate contained in the precipitate by the method described in the preceding section.^{21,22} The following method may be used for the determination of calcium in blood:²³

Reagents. *1-Amino-2-naphthol-4-sulfonic acid:* Dissolve 30 g. of sodium bisulfite and 1 g. of sodium sulfite in 200 ml. of water. Add 0.5 g. of pure 1-amino-2-naphthol-4-sulfonic acid and mix well. Filter, store in a dark bottle, and do not use after 2 weeks.

Standard phosphate solution: Dissolve 2.265 g. of pure monopotassium phosphate in water and dilute to 1 liter. Add a little chloroform as a preservative. One ml. of this solution is equivalent to 1 mg. of calcium. Transfer 10 ml. of this solution to a liter flask with a pipet and dilute to volume. One ml. of this solution is equivalent to 0.01 mg. of calcium.

Procedure. Add 2 ml. of blood serum to 8 parts of 10 per cent trichloroacetic acid and mix well. Filter and transfer 5 ml. of the filtrate to a centrifuge tube and add 1 ml. of 25 per cent sodium hydroxide solution. Mix and allow to stand for 5 minutes. With a high magnesium content a precipitate may form at this point. In this case, calcium and magnesium should be separated prior to the determination. If only small quantities of magnesium are present, add

1 ml. of 5 per cent trisodium phosphate solution, mix well, and allow to stand for 1 hour. Centrifuge for 2 minutes at 2000-2500 r.p.m. Decant the supernatant liquid and drain well, and then carefully wipe the liquid from the edge of the tube.

Prepare a wash solution as follows: mix 58 ml. of 95 per cent alcohol and 10 ml. of amyl alcohol in a 100-ml. graduated cylinder and dilute with water to 100 ml. Add 2 drops of 1 per cent phenolphthalein solution and neutralize the solution by the dropwise addition of 5 per cent sodium hydroxide solution. Only 2-3 drops of the base are usually required. Add 5 ml. of the neutralized alcoholic wash solution to the precipitate in the centrifuge tube and mix well with the precipitate with a glass rod. Centrifuge and decant the liquid as before. Again dry the edge of the tube, and add 1 ml. of acid molybdate containing 6.25 per cent ammonium molybdate in 1:4 sulfuric acid. When the precipitate has completely dissolved, add 10 ml. of distilled water and mix thoroughly.

Simultaneously with the preparation of the unknown, similarly treat 10 ml. of the standard containing phosphate equivalent to 0.01 mg. of calcium per ml. with ammonium molybdate. To both sample and standard add 5 ml. of the 1-amino-2-naphthol-4-sulfonic acid reagent and dilute to 15 ml. Mix well, and compare colorimetrically after 10 minutes.

Determination of silicon. King and Stantial²⁴ have recommended determining silicon by the reduction of silicomolybdic acid with 1-amino-2-naphthol-4-sulfonic acid. De Eds and Eddy,²⁵ however, claim that this method does not give satisfactory results. Recently, Olsen and coworkers²⁶ published a method for the determination of silica in leach liquors. This is reported to be satisfactory for rapid routine determinations, and has an accuracy of about 2 per cent.

Reagents. *Reducing reagent:* Dissolve 2 g. of 1-amino-2-naphthol-4-sulfonic acid, 120 g. sodium metabisulfite and 24 g. of sodium sulfite in distilled water and dilute to 1 liter. Store in dark bottle and in a cool place.

Ammonium molybdate: Dissolve 5 g. of ammonium molybdate in 100 ml. of water.

Standard silica solution: Dissolve 47.32 g. of sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, in 1 liter of water. This solution contains 10 mg. SiO_2 per ml. Filter and standardize gravimetrically.²⁷ Store in a rubber bottle.

Procedure. Transfer an aliquot of the acidified solution containing 0.02-0.10 mg. of silica to a 25-ml. calibrated blood-sugar test tube with the aid of a pipet. Add 2-3 drops of a saturated aqueous solution of 2,4- or 2,6-dinitrophenol, and pass ammonia gas (obtained by bubbling clean air through ammonium hydroxide) into the mixture to the yellow end point. Add 5 ml. of 0.5 N hydrochloric acid and dilute to the mark with distilled water. Mix thoroughly, and by means of a pipet add 2 ml. of ammonium molybdate solution. Again mix and allow to stand 5 minutes. Next add, with the aid of a pipet, 3 ml. of reducing solution. Mix thoroughly and determine the color absorption with the Klett-Summerson photoelectric colorimeter equipped with a filter having a transmission range of 640-700 μ . Make a blank determination on the reagents alone and apply a correction to the colorimeter reading.

To calculate the conversion factor, dilute 2 ml. of the standard silica solution to 1000 ml., and add 2 or 3 ml. of this solution to each of three 25-ml. blood-sugar tubes. Develop the color in each exactly as described above. Apply blank corrections, determine the average of the three readings, and evaluate the scale division in terms of mg. of silica.

Results obtained using this method are shown in Table 35. Straub and Grabowski²⁸ have used 1-amino-2-naphthol-4-sulfonic acid for the determination of silica in condensed steam in the presence of phosphates.

TABLE 35.—DETERMINATION OF SILICA WITH 1-AMINO-2-NAPHTHOL-4-SULFONIC ACID

Sample No.	SiO ₂ :Al ₂ O ₃ %	Total Silica		Error %
		Calcd. mg.	Found mg.	
1	0.1	0.0393	0.0392	+0.3
2	0.1	0.0590	0.0587	-0.6
3	0.1	0.0786	0.0778	-1.1
4	0.5	0.0590	0.0589	-0.2
5	1.0	0.0590	0.0590	0.0
6	1.0	0.0590	0.0590	0.0
7	1.0	0.0590	0.0596	+1.2
8	1.0	0.0590	0.0590	0.0
9	2.0	0.0590	0.0593	+0.8
10	3.0	0.0590	0.0593	+0.8
11	4.0	0.0590	0.0593	+0.8
12	5.0	0.0590	0.0593	+0.8

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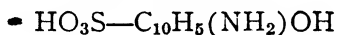
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1-AMINO-2-NAPHTHOL-6-SULFONIC ACID

$C_{10}H_9O_4NS$

Mol. Wt. 239.23

Beil. Ref. XIV, 847.



Use: Detection of potassium.

1-Amino-2-naphthol-6-sulfonic acid is a crystalline solid. It is slightly soluble in water and alcohol, and is insoluble in ether.

Detection of potassium. The sodium salt of 1-amino-2-naphthol-6-sulfonic acid has been proposed by Pinerua and Alvarez^{1,2,3} as a suitable reagent for the detection of potassium. The reagent is prepared by neutralizing the free acid with a solution of sodium hydroxide. This solution has a dark brown color, but when added to a neutral solution of a potassium salt, white, brilliant crystals of the potassium salt of the reagent are formed. The reaction is carried out by adding 4.5 ml. of a saturated solution of the sodium salt of the reagent to 0.5 ml. of unknown solution. The sensitivity of the reaction is about equal to that obtained with chloroplatinic acid, but the reaction is very slow. Ammonium chloride does not interfere. Magnesium chloride does not interfere in the presence of sufficient ammonium chloride to prevent its precipitation by carbonate. Iron and manganese are not precipitated. Lutz⁴ reports that the sensitivity of this reaction is about 1:1,000.

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o-AMINOPHENOL

C_6H_7ON

Mol. Wt. 109.12

Beil. Ref. XIII, 354.



Use: Detection of silver. Determination of gold.

o-Aminophenol occurs as white needles, which darken in air, especially when dissolved in water. The compound melts at 170° C. It is soluble in 59 parts of water at 0° C., and in 23 parts of alcohol, but is more soluble in ether.

Preparation: Place 20 g. of *o*-nitrophenol, 6 g. of sodium hydroxide, 5 g. of sulfur, 40 g. of sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and 100 ml. of water in a 500-ml. flask, and boil under reflux for 5 hours. Transfer to a beaker and add to the hot liquid, with stirring, a cold-saturated solution of sodium bisulfite until the mixture is acid to litmus. Chill the mixture and filter off the crude aminophenol.

Dissolve the impure product in the least possible quantity of 3 N hydrochloric acid and digest with charcoal. Filter into a 600-ml. beaker and add a concentrated sodium hydroxide solution until a partial separation of *o*-aminophenol occurs. Add carefully a saturated solution of sodium carbonate until all effervescence ceases and the mixture is distinctly alkaline to litmus. Cool in ice, filter off the *o*-aminophenol, and wash sparingly with ice water. Finally, purify by recrystallizing from hot water.¹

Determination of gold. Gold is precipitated quantitatively from solutions of gold compounds by reduction with *o*-aminophenol. This reagent may be used in place of hydroquinone for the determination of gold by the method of Beamish, Russell, and Seath² (page 135).

Detection of silver. Silver may be detected with *o*-aminophenol by means of a spot test.³ A 0.2 per cent solution of the reagent gives a reddish brown or dark yellow spot depending on the concentration of silver. The test is sensitive to 2 γ of silver. With 0.2 γ of silver a thin yellow ring is obtained.

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p-AMINOPHENOL

Synonym: 4-Aminohydroxybenzene, Rhodinal, Ursol P

$\text{C}_6\text{H}_7\text{ON}$

Mol. Wt. 109.12

Beil. Ref. XIII, 472.

$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{OH}$

Use: Detection of copper, cyanide, iron, magnesium, nitrite and vanadium.

Determination of gold.

p-Aminophenol consists of white to yellow or reddish crystals or powder which becomes violet on exposure to light. It melts at about 184° C. with decomposition. One gram of the solid dissolves in 90 ml. of cold water, or 22 ml. of cold absolute alcohol. It is also soluble in alkalis, and the resulting solutions rapidly become violet on standing. The compound is almost insoluble in benzene and chloroform.

p-Aminophenol hydrochloride, which is commonly used as the analytical reagent, is a white crystalline powder which gradually darkens with age. It melts at about 306° C. with decomposition. It is very soluble in water and is soluble in alcohol.

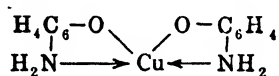
Preparation: Add 2.2 g. of phenylhydroxylamine in small portions to a mixture of 10 ml. of concentrated sulfuric acid and 30 g. of ice which is contained in a vessel surrounded by ice. Dilute the solution with 200 ml. of water and boil for about 10 to 15 minutes, or until a small sample no longer gives the odor of nitrosobenzene but of quinone when mixed with a solution of potassium dichromate. Neutralize the acid with sodium bicarbonate, saturate with salt, and extract with ether. The *p*-aminophenol is recovered as a crystalline solid by distilling off the ether.¹

Detection of copper and iron, silver and nickel. Augusti² first observed that blue-violet precipitates are obtained when a 2 per cent alcoholic solution of *p*-aminophenol hydrochloride is added to solutions of copper and iron salts. This reaction is used as a sensitive test for copper and iron.

Procedure. Add drop by drop 1-2 ml. of a 2 per cent alcoholic solution of *p*-aminophenol hydrochloride to a few ml. of the solution to be tested. A violet precipitate or turbidity indicates the presence of copper or iron. By means of this procedure as little as 0.15 mg. of copper or 0.013 mg. of iron can be detected.

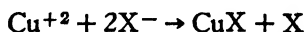
Other ions appear to cause no disturbance, and acetic acid makes the colors more intense. This reaction may be applied as a spot test by mixing drops of the solution to be tested and of the reagent solution on a spot plate. In this way as little as 0.2γ of copper at a concentration of 1:160,000, and 0.069γ of iron at a concentration of 1:360,440 can be detected.

According to Augusti² the composition of the blue-violet compounds of copper and iron correspond to inner-complex salts of the following composition:



Bogoslovskii and Krasnova³ have studied the reaction of *p*-aminophenol hydrochloride and copper, and explain the color reaction by assuming that cupric ions in the presence of sodium chloride catalyze the auto-oxidation of the reagent to produce a violet color which fades as a brown precipitate forms. They have studied this reaction with a view of adapting it to a colorimetric determination of copper, but they have reported that the violet color is not suitable for such determination.

Nazarenko⁴ claims that the reaction of *p*-aminophenol with copper and iron is neither catalytic nor complex forming, but rather is an oxidation reaction, at least in the first stage. According to this explanation the detection of copper is based upon the oxidation of *p*-aminophenol in the presence of a halide as a result of the reaction:



The oxidation products of *p*-aminophenol then form complex compounds with copper and iron. Nazarenko has reported that better results are obtained if potassium bromide is present.

According to Kulberg,⁵ the oxidation of *p*-aminophenol to a semiquinoid compound by copper salts in the presence of a halide results first in complex formation, with the consequent decrease of the cuprous ions in the $\text{Cu}^{++}/\text{Cu}^{+}$ equilibrium. The oxidation of *p*-aminophenol with ferric ions results in the direct exchange of electrons.

In a recent study, Kocsis and co-workers⁶ have applied reactions with *p*-aminophenol for the detection of copper, silver and nickel by means of spot tests. A 0.2 per cent solution of *p*-aminophenol is used and the spots are formed on filter paper, which is then dried. With solutions of rather high copper content, a grayish-blue spot is obtained, while with only 1 γ of copper an olive-green spot with a light brown border is formed. The ring starts from the original color of the reagent. Solutions of silver salts give a light brown spot with dark edges with as little as 0.4 γ of silver at a limiting concentration of 1:62,500. With nickel, *p*-aminophenol yields a blue-gray spot with a salmon colored border when as little as 0.4 γ of nickel is present. The limiting concentration is 1:62,500.

Detection of vanadium. *p*-Aminophenol is oxidized by means of potassium chlorate to a violet colored compound, although normally this reaction proceeds very slowly. In the presence of vanadium, however, this reaction is remarkably accelerated, and hence may be used as a means of detecting vanadium. The following procedure is taken from the work of Szebelledy and Ajtai.⁷

Procedure. Add 1 ml. of a 0.1 per cent solution of *p*-aminophenol and 1 ml. of a saturated solution of potassium chlorate to a little of the solution to be tested, contained in a test tube, and dilute to 5 ml. with distilled water. Prepare a second solution by mixing 1 ml. of a 0.1 per cent solution of *p*-aminophenol and 1 ml. of a saturated solution of potassium chlorate and dilute to 5 ml. with distilled water. Heat both tubes on a water bath for a few minutes and note the appearance of the two solutions. The tube containing only the reagents should remain colorless or pale pink, whereas a violet color appears in the second tube if as little as 0.1 γ of vanadium is present.

Lead must be absent since it interferes with the test. Ferrous and stannous salts also interfere but these may easily be eliminated. The above reaction is much more sensitive when carried out in the presence of a little 8-hydroxyquinoline.⁸ With this modification, as little as 0.01 γ of vanadium can be detected. Lead, copper, cadmium and $(\text{NH}_4)_2\text{SnCl}_6$ interfere.

Detection of magnesium. Eegriwe⁹ has used *p*-aminophenol as a reagent for detecting magnesium.

Procedure. To 1 drop of the solution to be tested add a few drops of concentrated ammonium hydroxide and a few crystals of solid *p*-aminophenol hydrochloride. Shake the mixture a few times and allow to stand. *p*-Aminophenol is slowly oxidized and the solution gradually becomes pale yellow and finally a light yellowish-brown. If magnesium is present, magnesium hydroxide is precipitated on the addition of ammonium hydroxide, and this adsorbs the dyestuff formed by the oxidation of the reagent and is gradually colored blue.

In this way approximately 0.2% of magnesium can be detected. All cations which yield precipitates with ammonium hydroxide interfere with this test.

Detection of nitrites. Thevenon¹⁰ has used *p*-aminophenol hydrochloride for the detection of nitrites in water.

Procedure. To 10-100 ml. of water to be tested add 2-3 ml. of a freshly prepared 0.5 per cent aqueous solution of *p*-aminophenol hydrochloride and 6-8 drops of 33 per cent acetic acid. A deep garnet-red color is formed if nitrites are present. Nitrates do not interfere.

Detection of cyanides. Koslovskii and Penner¹¹ have based a reaction for the detection of hydrogen cyanide upon its catalytic effect upon the reaction between ammonia and alloxan to form oxaluramide. *p*-Aminophenol has been substituted for ammonia in this reaction, but appears to offer no particular advantage in cyanide detection.

Determination of gold. *p*-Aminophenol can be used in a titration method for the determination of gold.¹² This is similar to that used with *p*-methylanilino-phenol (page 241).

Procedure. For determining quantities of gold ranging up to 5 mg., dissolve the metal in 2 ml. of aqua regia, and boil in a flask with rotation until only 1 or 2 drops of the liquid remain. Add 2 ml. of 1 per cent paraldehyde, blow the fumes from the flask, and allow to stand 2 minutes. Add 25 ml. of water and 1 ml. of 0.1 per cent *o*-tolidine solution in 10 per cent hydrochloric acid, and then add a small quantity of dilute silver nitrate solution as a catalyst. Titrate with 0.01 N *p*-aminophenol sulfate in 2 per cent hydrochloric acid. Heat the mixture gently during the titration.

In the presence of iron add ammonium fluoride. Large quantities of copper cause high results. *o*-Tolidine gives a yellow to brown color at a dilution as high as $1-2 \times 10^7$.

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2,4-DIAMINOPHENOL HYDROCHLORIDE

Synonym: Amidole

 $C_6H_8ON_2 \cdot 2HCl$

Mol. Wt. 197.07

Beil. Ref. XIII, 550.

 $HO \cdot C_6H_3(NH_2)_2 \cdot 2HCl$

Use: Detection of ammonia, chromium, copper, gold, nitrate, nitrite, and silicon. Determination of chromium, dissolved oxygen, gold, nitrate and nitrite.

This reagent is a gray-white, crystalline solid. It is soluble in water, but is only slightly soluble in alcohol.

Preparation. Reduce 1 part of 2,4-dinitrophenol with 4 parts of tin and 12 parts of hydrochloric acid. Filter, and to the filtered solution add a large excess of concentrated hydrochloric acid. After a time the hydrochloride separates as needle-like crystals. Filter, and wash with concentrated hydrochloric acid. Dissolve the precipitate in a little water, and again precipitate with concentrated hydrochloric acid. Filter, wash with concentrated hydrochloric acid, dissolve in dilute hydrochloric acid, filter, and allow the reagent to crystallize from the solution.¹

Detection and determination of nitrate and nitrite. An aqueous solution of 2,4-diaminophenol hydrochloride, slightly acidified with hydrochloric acid, produces a red-yellow coloration when added to a solution containing a nitrite. The sensitiveness of this reaction is 1:200,000.²

An intense red coloration is produced when a solution of the reagent in sulfuric acid is added to a solution of nitric acid or nitrate. The reagent is a freshly prepared solution formed by dissolving 2,4-diaminophenol hydrochloride, a little at a time, in concentrated sulfuric acid until a faint violet color is obtained.³ The sensitiveness of this reaction is 1:300,000.

Hydrochloric acid, hydrobromic acid, and hydroiodic acid interfere with this reaction and should be removed with mercurous sulfate. Potassium permanganate, chromates, dichromates, chlorates, and other oxidizing agents give the same reaction, but unlike nitrates, these substances also give a similar reaction with a solution of the reagent in concentrated hydrochloric acid.

Cernatescu and Gheller⁴ have used the above reaction for the colorimetric determination of small quantities of nitrates.

Detection and determination of gold. If 1 ml. of a 0.1 per cent solution of 2,4-diaminophenol is added to 10 ml. of a solution containing 0.002 per cent gold chloride, a violet color is obtained. This reaction is suitable for the detection of small quantities of gold.⁵

Gold is quantitatively precipitated from solutions of gold compounds by reduction with 2,4-diaminophenol hydrochloride. This reagent may be used in place of hydroquinone for the determination of gold (page 135).⁶

Determination of dissolved oxygen. 2,4-Diaminophenol hydrochloride in an alkaline solution is oxidized by dissolved oxygen to a stable, blue compound. The intensity of the color is directly proportional to the oxygen content of the solution.⁷ As reagent, use a solution prepared by dissolving 0.2 g. of

2,4-diaminophenol hydrochloride in 1 ml. of 0.1 N hydrochloric acid, adding a trace of sodium acid sulfite to remove any red color, and finally adding 25 ml. of glycerol.

Detection of ammonia. Diaminophenol reacts with ammonia to produce an intense yellow color.⁸ This reaction, which is said to be more sensitive than that with Nessler's reagent, can be used for the detection and colorimetric determination of ammonia.

Detection of copper. 2,4-Diaminophenol hydrochloride, like p-aminophenol (page 236), can be used for the detection of copper.⁹ The detection is based on the oxidation of the reagent, followed, perhaps, by the formation of a complex with the copper. The reaction detects 1 part of copper in one million parts of solution. Oxidizing agents interfere.

Detection of silicon. 2,4-Diaminophenol hydrochloride is one of the many reducing agents that may be used for the reduction of silicomolybdic acid as a test for silicon. A solution of the reagent containing sodium sulfite (to retard oxidation) may be used to detect 1 part of silicon in 200 million parts of solution. Slow but continuous oxidation of the reagent, however, produces a reddish-purple color which constantly changes, and this makes a quantitative comparison impossible.¹⁰

Detection and determination of chromium. A solution of 2,4-diaminophenol in concentrated sulfuric or hydrochloric acid yields a red color when added to a chromate. This reaction has been investigated as a possible method for the colorimetric determination of chromium.¹¹

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p-METHYLAMINOPHENOL

Synonym: Monomethyl-*p*-aminophenol, *p*-hydroxymonomethylaniline

C_7H_9ON

Mol. Wt. 123.14 Beil. Ref. XIII, 441 (149).

$HO-C_6H_4-NH(CH_3)$

Use: Detection of silver. Determination of gold and phosphorus.

The sulfate of *p*-methylaminophenol is sold as a photographic developer under the names of metol, photol, photo-rex and elon.

p-Methylaminophenol sulfate is a white crystalline solid. It becomes discolored in air and melts at 260° C. with decomposition. It dissolves in about 20 parts of cold water. It is only slightly soluble in alcohol and is insoluble in ether.

Preparation. *p*-Methylaminophenol sulfate is prepared by heating hydroquinone with an aqueous solution of methylamine in a sealed tube.¹

Determination of phosphorus. Small quantities of phosphorus may be determined colorimetrically by converting to the phosphomolybdate and reducing the latter to a blue compound with various reducing agents. Among the most common of the organic reducing agents used for this purpose are hydroquinone, benzidine and 1-amino-2-naphthol-4-sulfonic acid. *p*-Methylaminophenol sulfate may be used for this purpose with satisfactory results.^{2,3} A 3.128 per cent solution of *p*-methylaminophenol sulfate may be substituted for the 1 per cent solution of hydroquinone which is usually employed for the reduction of the phosphomolybdate. The color is developed in 20 minutes at 26-27° C. and is said to be clearer than when hydroquinone is used.³ Gomori⁴ claims that a reagent prepared by dissolving 1 g. of elon in 100 ml. of 3 per cent sodium bisulfite solution is better than other reducing agents which have been suggested for the phosphomolybdate reduction. Muller⁵ recommends a solution of elon in N sodium sulfite, but according to Gomori⁴ this reagent does not keep well and gives unsatisfactory results. Schnell and Frisch⁶ prepared the reducing reagent by dissolving 1 g. of *p*-methylaminophenol sulfate, 5 g. of sodium sulfite and 150 g. of sodium bisulfite in 500 ml. of water.

p-Methylaminophenol sulfate may be used for the determination of orthophosphate in the presence of meta- and pyrophosphate. The reaction is not given by metaphosphate or pyrophosphate, but when much of the latter is present, more molybdate must be used.⁷ *p*-Methylaminophenol sulfate has been used in procedures for the determination of phosphorus in plant ash^{3,6} and in blood serum.^{2,8}

Determination of gold. Gold may be determined volumetrically by titrating with a standard *p*-methylaminophenol chloride solution in the presence of *o*-tolidine.⁹

Reagent. Dissolve 1.284 g. of *p*-methylaminophenol hydrochloride in 1 liter of 2 per cent hydrochloric acid by volume. One ml. of this solution is equivalent to 1 mg. of gold.

Procedure. For determining up to 5 mg. of gold, dissolve the metal in a 200 ml. flask with 2 ml. of aqua regia. Heat until the sample is dissolved and then boil carefully, while rotating the flask, until only 1-2 drops of the liquid remain. Add 2 ml. of 1 per cent paraldehyde solution, blow out the fumes from the flask and allow the mixture to stand for 2 minutes. Add 25 ml. of water, 1 ml. of 0.1 per cent *o*-tolidine in 10 per cent hydrochloric acid and a little dilute silver nitrate solution as a catalyst. Titrate carefully with the 0.01 N reagent

solution in 2 per cent hydrochloric acid. The yellow color is discharged by titration with the reagent. When the yellow color has disappeared, heat to 40° C., and any slight yellow color is then discharged by further titration.

If iron is present, add a little ammonium fluoride. If large quantities of copper are present, the results obtained are high.

Detection of silver. One of the most satisfactory methods for detecting small quantities of silver is based on the formation of silver bromide and its subsequent reduction with a developing solution containing p-methylaminophenol and a silver salt.^{10,11,12} This test is carried out as follows:

Reagent. Dissolve 10 g. of p-methylaminophenol and 50 g. of citric acid in 500 ml. of water. To 50 ml. of this solution add 2 ml. of 0.1 M silver nitrate solution immediately before use.

Procedure. Draw a circle about 0.5 inch in diameter on a piece of Whatman 120 or 42 filter paper, and in the center of this circle place a drop of the very dilute solution to be tested. Place the paper in a shallow dish and cover with a 0.02 N solution of potassium bromide and allow to stand 30 seconds. Pour off the potassium bromide solution and replace with distilled water. Shake the dish and change the water every 30 seconds until the paper has been washed 6-8 times. When the final wash water has been removed, the reagent solution is poured in the dish. After a time a gray to black spot appears within the circle depending on the silver concentration. As long as 30 minutes may be required for the development of the test. With very dilute silver solutions, the reagent solution may become cloudy before a positive test is obtained. Should this occur, remove the paper, wash thoroughly and treat with a fresh reagent solution. With this test 0.005% of silver may be detected at a dilution of 1:10,000,000.

All reagents and equipment used in this test must be very clean. It is also important that all potassium bromide be washed from the paper before treatment with the reagent solution.

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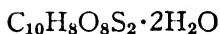
CHAPTER XII

PHENOL SULFONIC ACIDS

A number of phenolsulfonic acids have been used in analytical reactions. Many of these, which contain other functional groups in addition to the phenolic and sulfonic acid groups, are listed in other chapters; but a few which owe their analytical usefulness to their phenol characteristics are included here. A number of these compounds, such as phenoldisulfonic acid, are used for the detection and determination of nitrate. Others, such as chromotropic acid and 1,2-dihydroxybenzene-3,5-disulfonic acid possess structures capable of forming chelate rings with metal atoms.

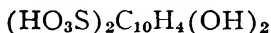
1,8-DIHYDOXYNAPHTHALENE-3,6-DISULFONIC ACID

Synonym: Chromotropic acid



Mol. Wt. 356.32

Beil. Ref. XI, 307



Use: Detection of chlorate, chromium, mercury, nitric acid, nitrous acid, oxidizing agents, silver and titanium.

Determination of chromium and titanium.

Chromotropic acid is a white crystalline solid, which is very soluble in water. The disodium salt, which is the form in which the reagent is generally used, crystallizes in the form of white needles or leaflets with two molecules of water of hydration. It is very soluble in water.

Detection of titanium. Chromotropic acid reacts with solutions of titanium salts, titanium hydroxide, and titanic acid in hydrochloric and sulfuric acid solutions to give a red-brown color. A similar reaction is not obtained in solutions containing a high concentration of nitric acid.¹⁻⁴ The composition of the colored product is not definitely known, but it appears probable that, owing to the relationship of the hydroxyl groups, the compounds formed are similar to those obtained in the reaction with pyrocatechol (page 000).

This reaction may be used as the basis for a sensitive test for titanium.^{1,2,5}

Procedure. Place a drop of the solution to be tested on a strip of filter paper, or on a spot plate, and mix with a drop of a 5 per cent solution of the reagent. An intense brown coloration appears if titanium is present. As little as 5γ of TiO_2 may be detected if present in a concentration of 1:10,000.

According to Vanossi⁶ this reaction is more sensitive than those employing thymol and hydrogen peroxide. With suitable precautions 0.5γ of titanium can be detected in pure solutions; 0.5-1.5γ can be detected in the presence of most

other metals; and 3-5 γ in the presence of columbium, chromium, phosphorous, tantalum, tellurium or tungsten. Kuznetsov⁷ states that tetravalent titanium reacts with chromotropic acid while trivalent titanium does not. This suggests a method for the differentiation of the two valence states.

A number of metal salts may interfere with the titanium reaction, and consequently special precautions must be taken in analyzing a solution which may contain a mixture of ions. Ferric salts yield a deep green color and uranyl salts give a brown color. These colors, however, are easily destroyed by the addition of a little stannous chloride in hydrochloric acid, since ferrous and uranous salts, which are formed by reduction with stannous chloride, do not give a color reaction with the reagent. Dissociated mercury salts give a yellowish color, and silver salts a black color when treated on the spot paper with a solution of the reagent. The presence of these two salts, however, does not necessarily cause interference with the titanium reaction, since the color due to titanium is still perceptible. The same may also be said of iron, since the titanium color usually forms as a brown-red spot in the center of a green stain. In many cases, however, uncertainty may arise concerning the titanium test, and in these cases the following procedure should be used:

Procedure. Place a large drop of the solution to be tested on a watch glass and mix with stannous chloride, taking care to avoid a large excess of this reagent, and heat gently. Place a drop of 5 per cent chromotropic acid solution on a strip of filter paper, and to this add a drop of the clear solution from the watch glass. In the presence of titanium a red-brown color appears. The precipitate, as well as the clear solution from the watch glass, may be placed on the filter paper, since the precipitate remains at the point where it is deposited, while the solution diffuses into a zone surrounding it. In this case the moist zone is treated with the chromotropic acid solution, and if titanium is present, a reddish-brown circle appears about the precipitate.

Ballaban⁸ has improved this procedure somewhat by using a solution of chromotropic acid in concentrated sulfuric acid. Using this solution, only large amounts of colored metal salts, nitrates or other oxidizing agents interfere. The latter may be removed by heating with concentrated sulfuric acid until fumes appear.

Procedure. Mix a drop of the solution to be tested in sulfuric acid on a spot plate with 5 drops of a solution prepared by dissolving 0.02 g. of chromotropic acid in 20 ml. of concentrated sulfuric acid. A violet color appears if titanium is present. If only small quantities of titanium are present, it is best to make a blank test. In this way 0.1 γ of titanium may be detected. The concentration limit is 1:500,000.

With the use of stannous chloride, titanium may be detected in the presence of uranium salts.⁹

Procedure. Treat a little of the solution to be tested with a slight excess of stannous chloride and heat to boiling. Filter or decant, and add a little 5 per cent solution of the reagent to the filtrate. A cherry-red or a reddish-brown color

appears depending upon the concentration of the titanium in the solution. The color is discharged on the addition of nitric acid.

While stannous chloride does not prevent the reaction between titanium and chromotropic acid, a large excess weakens somewhat the color of the titanium compound. Consequently, for maximum sensitivity it is important to avoid a large excess of the stannous chloride reagent.

Tananaev and Panchenko² have applied the chromotropic acid reaction of titanium salts to the detection of titanium in such minerals as rutile, kaolin, monazite, etc. The following procedure is used:

Procedure. Finely powder the mineral to be analyzed, and mix a portion about the size of a head of a pin with 3-4 times that quantity of potassium bisulfate and melt on a strip of platinum. Transfer the melt to a watch glass, mix with a little water, and transfer to a strip of filter paper which has been impregnated with chromotropic acid solution. A red to red-brown color appears if titanium is present.

This test is made more sensitive by adding a drop of hydrochloric acid solution of stannous chloride to the melt on the watch glass, and then adding a few drops of the chromotropic acid reagent. If titanium is present, not only the dissolved, but also the undissolved particles are turned red.

Feigl has modified this procedure somewhat by mixing the finely powdered sample with a few drops of concentrated sulfuric acid and then heating to fuming in a microcrucible or a test tube. The test is made on the cooled mixture by adding a small particle of solid chromotropic acid, followed by gentle warming. A more or less intense violet color appears if titanium is present. Traces of titanium in silicates, such as glass, may be detected by the following procedure:

Procedure. Treat a few milligrams of the powdered sample with hydrofluoric acid in a platinum dish, and then heat with 2 or 3 drops of concentrated sulfuric acid. Transfer this mixture to a test tube using a little concentrated sulfuric acid, and then complete the test with chromotropic acid as described above.

Thanheiser¹⁰ and Evans¹¹ suggested a method for detecting titanium in steel without dissolving a sample of the metal. The surface of the steel is cleaned thoroughly and treated with a drop of hydrochloric acid. The resulting drop is transferred to a spot plate or taken up with a sheet of filter paper and tested with chromotropic acid in the usual manner.

Determination of titanium. The color formed by the action of titanium and chromotropic acid may be used for the colorimetric determination of titanium in cast iron, steel, slags and similar materials.

Thanheiser¹² recommends chromotropic acid as the best means of determining titanium in solutions containing tantalum. This reagent is particularly useful when the tantalum is to be determined with pyrogallol, since titanium interferes with the latter reaction by giving the same color as tantalum with pyrogallol. The following procedure has been suggested by Panchenko and Raetzkii.¹³

Procedure. Dilute 5-10 ml. of a solution previously reduced with amalgamated zinc to 50 ml., and add to this 2 ml. of a 2 per cent aqueous solution of chromotropic acid. Compare the resulting color with that obtained with a 0.001 N titanium solution.

With solutions containing 5-20 mg. of titanium per 100 ml. an error of only 0.03 per cent is obtained.

According to Lenher and Crawford,¹⁴ chromotropic acid is capable of detecting 0.01 mg. of TiO_2 , but is not satisfactory for the colorimetric determination of titanium. A study of this method has been carried out by Endredy and Brugger.¹⁵

Detection and determination of chromium. An aqueous solution of chromotropic acid reacts with chromic anhydride, chromates, and dichromates to yield very sensitive colors, which vary from cherry-red to purple.¹⁶ A deep red color is obtained with as little as 0.0008 mg. of chromium as chromate. This reaction is more sensitive than those with benzidine, pyrogalloldimethylether, diphenylcarbazide acetate, and α -naphthylamine.¹⁶

The color reaction obtained when chromotropic acid is added to solutions of chromates that have been acidified with sulfuric and phosphoric acids may be used for the colorimetric determination of chromium.¹⁷⁻²⁰ This pink color is so delicate that 0.001 per cent of chromium can be determined in a 2 g. sample. There is no advantage to using this method when more than 0.6 per cent chromium is present. This method is particularly useful for the determination of chromium in iron and steel. The following method has been recommended by Appelbaum.¹⁸

Procedure. If the steel to be analyzed contains 0.01-0.1 per cent of titanium, use 0.4 g., or if it contains 0.1-0.2 per cent titanium, use 0.2 g. of the sample, and dissolve in 10 ml. of 1:3 sulfuric acid contained in a 300-ml. flask. When solution is complete, add 0.5 ml. of concentrated nitric acid and heat until the mixture fumes. Then cool and add 50 ml. of water and 50 ml. of 10 per cent sodium hydroxide and 1 g. of sodium peroxide. Boil about 5 minutes, or until the excess sodium peroxide is destroyed. Cool the mixture to room temperature, and dilute to 200 ml. in a calibrated flask. Filter off 100 ml. of this solution and add 2 ml. of 85 per cent phosphoric acid and 8 ml. of concentrated sulfuric acid, and then immediately add 2 ml. of a 1 per cent solution of the sodium salt of chromotropic acid. Mix well and allow to stand for 15 minutes and then compare with standards similarly prepared.

The comparison may be made by the dilution method only, because of the peculiar character of the color developed and the danger of interference.

The standard is simultaneously and similarly prepared from a steel of known chromium content. The standard may also be prepared by adding a known quantity of potassium dichromate to a solution of chromium-free steel. The final dilution should be such that 1 ml. of solution contains 1.0 mg. of chromium.

Considerable quantities of vanadium may interfere by causing the appearance of a brown color. If the quantity of vanadium present is less than that of

chromium, a correction may be applied as follows: subtract from the percentage of chromium obtained one third of the percentage of vanadium present as determined by a separate analysis. This gives the correct percentage of chromium present. If the ratio of chromium to vanadium is high, the error is small and may be neglected. Interference by vanadium may also be eliminated by adding the same amount of vanadium to the standard as is contained in the sample.

Interference by iron is prevented by the presence of phosphoric acid. Molybdenum and tungsten do not interfere. Titanium is removed in the determination. The average error is less than 1 per cent.

A method similar to that described above has been used by Scott,¹⁹ who dissolved the sample of steel in perchloric acid.

Procedure. Dissolve 0.2-0.4 g. of the sample in 10 ml. of 60 per cent phosphoric acid. Heat until the mixture fumes, cool, and add 15 ml. of water and boil to remove the chlorine. Add 50 ml. of cold water and 50 ml. of 10 per cent sodium hydroxide solution and again boil. Cool and dilute to 200 ml. Filter and to 100 ml. of the filtrate add 8 ml. of concentrated sulfuric acid, 2 ml. of 85 per cent phosphoric acid and 2 ml. of 1 per cent solution of the reagent. Allow to stand 15 minutes and compare the resulting pink color with that of standards similarly prepared.

Garratt¹⁷ claims that as little as 0.001 per cent of chromium can readily be determined by this method, which is recommended for materials containing less than 0.6 per cent of chromium.

Koenig²⁰ has applied this method to the determination of chromium in plant ash.

Procedure. Ash 5 g. of dried plant material and dissolve the ash in 40 ml. of water. Add 1 ml. of syrupy phosphoric acid and dilute to 50 ml. To 10 ml. of this solution add 1 ml. of a 0.1 per cent solution of the disodium salt of 1,8-dihydroxynaphthalene-3,6-disulfonic acid and allow to stand 15 minutes. Compare the resulting color with that of a standard prepared from chromium-free plant ash to which is added a standard solution of chromate or dichromate. The standard should be similarly and simultaneously treated. The comparison should be repeated on the following day.

Klinger and co-workers²¹ have used a similar method for the photometric determination of chromium in tantalum metal.

Detection of mercury and silver. Kocsis and Gelei²² have used chromotropic acid for the detection of mercury and silver. The reaction gives a brown precipitate with solutions of mercurous salts, and a bright yellow precipitate or color with solutions of mercuric compounds. With silver ions a white precipitate is formed, and this rapidly darkens on standing. The test is best carried out by adding a drop of the solution to be analyzed to filter paper which has been impregnated with a drop of a freshly prepared 5 per cent chromotropic acid solution. A fairly sharp color reaction is obtained with as little as 0.2 mg. of the silver, mercurous or mercuric ion. Iron also may interfere. The reaction is sensitive to 10 p.p.m. of mercury.²³

Detection of oxidizing agents. Solutions of nitrates, ferric chloride, chlorates, nitrous acid and other oxidizing agents in sulfuric acid react with an aqueous solution of chromotropic acid to yield colored products. The following method may be used for the detection of nitrates.²⁴

Procedure. Mix 5 ml. of the solution to be tested with 5 ml. of concentrated sulfuric acid, and add a drop of an aqueous solution of chromotropic acid. A red or orange color appears depending upon concentration of nitrate. The coloration is obtained with as little as 0.15 g. KNO_3 per liter of solution.

Alkalimetry and acidimetry. A dilute aqueous solution of chromotropic acid in filtered ultra-violet light exhibits a characteristic light blue fluorescence, which increases with the concentration of the reagent. This fluorescence is increased by the addition of hydroxyl ions. Since the slight fluorescence obtained in alkaline solutions disappears on adding an acid, titrations of hydrochloric acid against sodium hydroxide and potassium bicarbonate can be satisfactorily carried out in ultraviolet light, using the fluorescence as an indicator.²⁵ This procedure may have some application in exact neutralizations in which the presence of an internal indicator is objectionable.

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1,2-DIHYDROXYBENZENE-3,5-DISULFONIC ACID

Synonym: Catechol disulfonic acid



Mol. Wt. 270.23

Beil. Ref. XI, 297

**Use:** Detection of iron and titanium. Determination of iron and titanium.

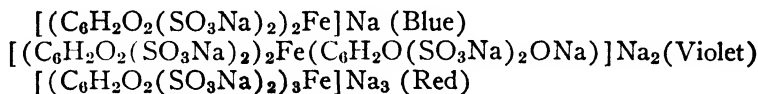
1,2-Dihydroxybenzene-3,5-disulfonic acid is a crystalline mass which dissolves readily in water and alcohol.

Preparation: Mix 1 part of pyrocatechol and 5 parts of fuming sulfuric acid (30 per cent) and heat at 100° C. for one-half hour.

Detection and determination of iron. The disodium salt of 1,2-dihydroxybenzene-3,5-disulfonic acid, like pyrocatechol and many other o-dihydroxybenzene derivatives, reacts with ferric iron to yield highly colored complexes. In an alkaline solution of pH 9-10, a red color is obtained which is detectable at a dilution of 1:200,000,000 when observed in a 50-ml., tall-form Nessler cylinder; in an acid solution of pH 3.5-4.5 a blue color is obtained and is sensitive to 1 part in 30,000,000. Both colored complexes obey Beer's law over a useful range of iron concentrations from 0.2-10 p.p.m. Not only is the reagent extraordinarily sensitive, but it is remarkably free of interference by other ions. Ferric iron may be determined colorimetrically with this reagent in the presence of fluoride, phosphate, tartrate and oxalate, which normally interfere seriously with colorimetric iron determinations.

The color reaction with iron is practically specific, since no other ion produces a blue or red color with the reagent. The iron complex is very soluble in water and is stable to light. The reagent is colorless in aqueous solution, and an excess produces no change in the color of the complex.

In acid solutions of pH below 5, the ferric complex is deep blue in color. If the solution is made alkaline, the color changes sharply to violet at pH 5.5-6.5 and becomes red at pH 7. This change in color appears to be caused by a change in the ratio of the pyrocatechol groups to iron as the hydrogen ion concentration is changed. The composition of the complexes is believed to be



Optimum concentrations for the visual study of the red complex are within the range 0.0-2.0 p.p.m. of iron. The region of greatest sensitivity between fixed small increments is in the range 0.08-0.12 p.p.m. Within this range solutions differing from each other by 1 part in 100,000,000 may be identified with certainty. At concentrations of approximately 1 p.p.m., the color intensity of the red complex prevents detection of differences much greater than 1:50,000,000. Differences of 1 p.p.m. of iron may be detected by the blue complex. Since the intensity of the blue color is less than that of the red, the optimum range for the detection of iron with this color is somewhat less than 1 p.p.m.

The following method may be used for the detection of iron:¹

Reagent solution. Dissolve 0.129 g. of the disodium salt of 1,2-dihydroxybenzene-3,5-disulfonic acid in distilled water and dilute to 100 ml.

Buffer Solution. Dissolve 136 g. of sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, and 66.6 ml. of 12 N hydrochloric acid in water and dilute to 2 liters. The pH of this solution is 4.0.

Procedure. Transfer 0.05 ml. of the solution to be tested to the depression of a spot plate and add 0.05 ml. of the reagent and 0.05 ml. of the buffer solution. This test is sensitive to 0.05% of iron.

Color reactions obtained with other ions are shown in Table 36.

TABLE 36.

Ion	Color	Remarks
MoO_4^{2-}	Yellow	Alkaline solution
OsO_4^{2-}	Yellow	
Cu^{+2}	Greenish-yellow	
UO_2^{+2}	Yellow	
VO^+	Purple	Fades to colorless within 15 minutes.
Ti^{+4}	Intense yellow	

Silver and chloroauric ions are reduced to the metal by the reagent. Only ferric ions produce either a blue or red color. The following method may be used for the colorimetric determination of iron:¹

Reagents. *1,2-Dihydroxybenzene-3,5-disulfonic acid (disodium salt):* Dissolve 0.269 g. of the reagent in distilled water and dilute to 1 liter.

Sodium acetate-hydrochloric acid buffer. Dissolve 136 g. of sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, and 66.6 ml. of 12 N hydrochloric acid and dilute to 2 liters. The pH of this solution is 4.

Phosphate buffer. Dissolve 71.6 g. of disodium phosphate, $\text{NaHPO}_4 \cdot 12\text{H}_2\text{O}$, in water, add 4 ml. of N sodium hydroxide and dilute to 1 liter. The pH of this solution is 9.5.

Procedure. Weigh a sample containing not more than 1 mg. of iron and dissolve by appropriate treatment, using either a fusion method or treatment with mineral acids or both. Remove interfering ions by the usual methods of separation. Transfer the sample solution to a 100-ml. volumetric flask and dilute to the mark with water. Mix thoroughly and transfer a 5-ml. aliquot to a 50-ml. tall-form Nessler cylinder. Add 1 ml. of the reagent and dilute to the mark with either sodium acetate-hydrochloric acid or phosphate buffer, depending on whether the red or blue complex is to be matched. Mix thoroughly and compare

with standards buffered to the same pH and covering the same range of concentration.

Detection and determination of titanium. The disodium salt of 1,2-dihydroxybenzene-3,5-disulfonic acid reacts with titanium salts to form a bright lemon-yellow color. This reaction is sensitive to 1 part of titanium in 100,000,000 parts of solution when observed in 50-ml. tall-form Nessler tubes. The color intensity of the complex is independent of acidity at pH 4.3-10, and obeys Beer's law over a useful range of titanium concentrations. Aluminum, calcium and tungsten ions reduce the color intensity, but this difficulty is largely eliminated by adding more of the reagent. Iron, vanadium and uranium interfere by forming colors with the reagent. Interference by iron may be eliminated by buffering the solution to pH 4.7 with acetic acid and sodium acetate, and adding 50 mg. of $\text{Na}_2\text{S}_2\text{O}_4 \cdot \text{H}_2\text{O}$ per 100 ml. of solution.²

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HYDROQUINONESULFONIC ACID

$\text{C}_6\text{H}_6\text{O}_5\text{S}$

Mol. Wt. 190.17

Beil. Ref. XI, 300

$\text{HO}_3\text{S} \cdot \text{C}_6\text{H}_3(\text{OH})_2$

Use: Detection and determination of nitric acid.

Hydroquinonesulfonic acid is a white deliquescent solid which dissolves readily in water.

Determination of nitrates. Hydroquinonesulfonic acid reacts with nitric acid, and yields, according to the nitrate content, a bright green to brownish-green color. This method has been used by Bini^{1,2} for the detection and colorimetric determination of nitric acid. The following method may be used for the detection of nitrate in water:

Reagent. Warm 5 g. of hydroquinone with 7.5 g. of concentrated sulfuric acid for 10 minutes on a water bath until crystallization begins at 90-100° C. Cool, and after 2-3 hours a white crystalline mass is formed. Dissolve in double-distilled water and use as the reagent.

Procedure. In a 50-ml. cylinder mix 10 ml. of water to be analyzed with 0.5 ml. of reagent solution and carefully add 20 ml. of pure concentrated sulfuric acid. Allow the mixture to stand for not more than 5 minutes and compare with a solution prepared with double-distilled water.

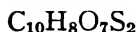
This reaction is sensitive to 0.01 mg. of nitrate per liter, and nitrites in concentration up to 0.2 mg. per liter do not interfere. Large quantities of chlorides do not interfere but chromates and hydrogen peroxide react in the same way as nitrates. Ferric salts give a bluish violet color but this disappears on the addition of sulfuric acid. Bini^{1,2} claims this method has the advantage over many

others which have been used in that it is sensitive and free from interference by nitrites.

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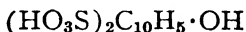
2-NAPHTHOL-6,8-DISULFONIC ACID

Synonym: "G acid"



Mol. Wt. 304.28

Beil. Ref. XI, 290 (67)



Use: Detection of nitrate and nitrite.

2-Naphthol-6,8-disulfonic acid is a white crystalline solid which dissolves readily in water. The potassium and sodium salts of this acid are known as "G salt."

Preparation: Add 1 part of β -naphthol to 5 parts of concentrated sulfuric acid that has been cooled to 0° C., and during the course of 36 hours gradually elevate the temperature to 60° C.

Detection of nitrites and nitrates. Nitrates and nitrites yield a wine-red to yellow color when treated with 2-naphthol-6,8-disulfonic acid in the presence of sulfuric acid. This reaction has been used by Nixon¹ for the detection of nitrites and nitrates.

Procedure. To 1 ml. of the solution to be tested, add 1 ml. of concentrated sulfuric acid and 5 ml. of 1 per cent aqueous solution of 2-naphthol-6,8-disulfonic acid. A distinct red color appears with 0.02 mg. nitrogen as nitrate, and a yellow coloration forms with less nitrate.

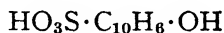
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1,5-NAPHTHOLSULFONIC ACID



Mol. Wt. 224.22

Beil. Ref. XI, 273.



Use: Detection and determination of nitric acid.

1,5-Naphtholsulfonic acid is a deliquescent crystalline solid which melts between 110-120° C.

Preparation: A reagent suitable for the detection of nitrates is prepared by heating 200 ml. of sulfuric acid on a water bath for one-half hour, then adding 20 g. of α -naphthol, and heating on the water bath for an additional hour.

Detection and determination of nitrates. When a solution of 1,5-naphtholsulfonic acid in sulfuric acid is added to a small quantity of a nitrate and the resulting solution is made alkaline, an intense yellow color appears. Murty^{1,2,3}

has studied the use of this reagent for the colorimetric determination of small quantities of nitrates. According to these studies, 1,5-naphtholsulfonic acid can replace phenolsulfonic acid for this purpose. The color reaction is carried out according to the following procedure:²

Procedure. Evaporate to dryness 25 ml. of a solution containing not more than 0.01 mg. of nitrate nitrogen per ml. Add 2 ml. of the reagent prepared as described above (see section on preparation), and allow to stand 15 minutes. Dilute the solution somewhat with water and add 8 ml. of 10 N sodium hydroxide solution. Dilute to 250 ml.; and, if the color is too intense, dilute a suitable aliquot with distilled water. The resulting color is compared with standard solutions prepared as described above in which exactly 0.01 mg. of nitrogen as nitrate is used.

If more than 1 p.p.m. of nitrite is present, the results obtained by the above procedure are too high. A study of the phenolsulfonic acid method and the 1,5-naphtholsulfonic acid method indicates that the latter reagent is preferable, and the effect of nitrite can best be eliminated by treating with urea, which decomposes the nitrite without affecting the nitrate.⁴ The solution to be analyzed is treated with an excess of a 1 per cent urea solution and 4-5 drops of 0.002 N sulfuric acid. From this point the procedure is carried out as described above. The color obtained in the reaction of nitrates with 1,5-naphtholsulfonic acid is not stable for more than 6 hours. Murty³ has found that an 0.08 N ferric chloride solution has exactly the same color obtained with a solution containing 0.25 mg. of nitrogen as nitrate; hence, ferric chloride solutions have been recommended as satisfactory permanent color standards for the nitrate determination.³ With solutions of the same nitrate content, 1,5-naphtholsulfonic acid gives colors with a longer dominant wave length and with greater brightness than with phenolsulfonic acid. With solutions containing less than 1 mg. of nitrate nitrogen, 1,5-naphtholsulfonic acid is recommended as the more satisfactory reagent, and with higher concentrations phenolsulfonic acid is recommended.¹

Vagi⁵ has used 1,5-naphtholsulfonic acid for the detection of small quantities of nitrate.

Procedure: Mix 5 ml. of the solution to be tested with 5 ml. of concentrated sulfuric acid and 1 drop of aqueous solution of 1,5-naphtholsulfonic acid. A wine-red color appears if nitrates are present. This color is obtained with as little as 0.15 g. of potassium nitrate per liter.

Ferric chloride, chlorates, nitrous acid and other oxidizing agents give a similar color.

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NAPHTHOLTRISULFONIC ACID

Synonym: 1-Hydroxy-2,4,8-trisulfonic acid

 $C_{10}H_8O_{10}S_3$

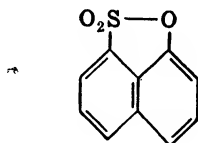
Mol. Wt. 384.34

Beil. Ref. XI, 280 (66).

 $(HO_3S)_3C_{10}H_4-OH$ **Use:** Detection and determination of iron.

The sodium salt of naphtholtrisulfonic acid is readily soluble in water but only slightly soluble in alkalis. Its aqueous solution exhibits an intense green fluorescence.

Preparation: Diazotize 1-naphthylamine-8-sulfonic acid and heat with water to form the compound:



Add this to 5 parts of fuming sulfuric acid of 25 per cent sulfur trioxide content while cooling in ice. Allow to stand 1-2 days at room temperature and then pour into ice water. Neutralize with calcium hydroxide, filter, and treat the filtrate with sodium carbonate. Filter and evaporate until a test portion when acidified with hydrochloric acid yields a crystalline paste. The sodium salt separates as a sandy powdered compound.^{1,2,3}

Detection and determination of iron. An aqueous solution of the sodium salt of naphtholtrisulfonic acid when added to a solution containing the ferric ion yields a deep blue color which may be used for the detection and colorimetric determination of ferric ion. The compound has the structure $Fe(RO_4)^{+2}$, in which RO^- represents the anion of the phenolic compound.⁴

1. H. Erdmann, *Ann.* **247**, 321, 343, 345 (1888).
2. G. Schultz, *Ber.* **20**, 3162 (1887).
3. O. Dressel and R. Kothe, *Ber.* **27**, 2144 (1894).
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PHENOLDISULFONIC ACID

Synonym:

1,2,4-phenoldisulfonic acid, phenol-2,4-disulfonic acid, phenolsulfonic acid

 $C_6H_6O_7S_2$

Mol. Wt. 254.23

Beil. Ref. XI, 250.

 $(HO_3S)_2C_6H_3-OH$ **Use:** Detection of nitrate. Determination of nitrate, and potassium.

Phenoldisulfonic acid consists of colorless deliquescent needles. It melts when heated and decomposes above 100° C. It is very soluble in water and alcohol, but is insoluble in ether.

Preparation: Phenoldisulfonic acid is prepared by heating phenol with fuming sulfuric acid, and is used without separating the pure compound from the excess sulfuric acid. The preparation of the sulfuric acid solution will be described under the procedure describing its use.

Detection and determination of nitric acid. Solutions containing nitrates give a yellow color with a reagent prepared by treating phenol with fuming sulfuric acid. This color is intensified when the solution is made alkaline. The use of phenoldisulfonic acid for the detection and determination of nitric acid was first proposed by Sprengel¹ in 1863, who concluded that the yellow color was due to the formation of picric acid. This reaction was observed by Kekule,²⁻⁸ and was later established as the practical basis for the determination of nitrates by Grandval and Lajoux.^{9,10} The method proposed by Grandval and Lajoux is essentially the same as that used today, although it has subsequently undergone various modifications.¹¹⁻¹⁷ The yellow color was believed to be due to the formation of an alkali picrate. Hazen and Clark,¹⁸⁻²¹ however, showed that the yellow color could not be that of an alkali picrate and concluded that it was due to the formation of mononitrophenols. Montanari²²⁻²⁵ believed that dinitrophenol was formed. The reaction was also studied by Gill,^{26,27,28} who attempted to prepare a reagent of definite composition. In 1910 Chamot and Pratt^{29,30,31} proved that the yellow color is due to the formation of the tripotassium salt of nitrophenoldisulfonic acid. Furthermore, they have given directions for preparing a reagent which consists essentially of 1,2,4-phenoldisulfonic acid.

If conditions are not carefully standardized for the preparation of the phenolsulfonic acid reagent, it contains mono-acids, and is never satisfactory for the nitrate determination, since it changes with age, and is seriously influenced by variation in concentration and temperature during the determination. Further, such reagent cannot be employed satisfactorily with permanent standards.

o-Phenolmonosulfonic acid gives an intense grass green color when the reagent is poured over dried nitrate, diluted, and made alkaline. The color is so intense that it may be observed if more than 5 parts of nitrogen are present in 1,000,000 parts of solution. The *p*-phenolmonosulfonic acid gives similar results but only upon heating. Prolonged heating of nitrates with the reagent gives in both cases, after treatment with an excess alkali, a yellow solution which possesses a greenish tint. 1,2,4-Phenoldisulfonic acid when added to nitrates and made alkaline gives a pure yellow solution with practically no trace of green. This reaction, however, is less delicate than that with the *o*-phenolmonosulfonic acid. No other compound giving a yellow color with alkalis could be isolated. Only traces of picric acid were present when the nitrate content exceeded 50 p.p.m. Somewhat larger quantities of picric acid are formed on long heating.

A reagent containing only phenoldisulfonic acid may be prepared according to the method described by Chamot, Pratt and Redfield.²⁹

Procedure. Dissolve 25 g. of colorless phenol in 150 ml. of pure concentrated sulfuric acid. Sulfuric acid frequently contains traces of nitric acid but this can be removed by agitating with mercury.³² Add 75 ml. of fuming sulfuric acid containing 13 per cent of free sulfur trioxide. Stir well and heat in a flask for 2 hours on a boiling water bath.

The reagent prepared according to the above directions contains no mono- or trisulfonic acid and may be heated in contact with a residue obtained by evaporating water for 4 hours without the appearance of interfering colors. Sulfonation is usually complete in about 1 hour, but a longer heating period insures the absence of monosulfonic acid.

The following procedure for the determination of nitrates in water by the phenoldisulfonic acid method is recommended by the American Public Health Association.³³

Reagents. *Phenoldisulfonic acid reagent:* This reagent is prepared according to the method of Chamot, Pratt and Redfield described above.

Potassium hydroxide solution: Prepare an approximately 12 N solution of potassium hydroxide. Ten ml. of this reagent will neutralize about 4 ml. of the phenoldisulfonic acid reagent.

Standard nitrate solution: Dissolve 0.7216 g. of pure recrystallized potassium nitrate in 1 liter of distilled water. Evaporate 50 ml. of this solution to dryness on a water bath and quickly moisten the residue with 2 ml. of phenoldisulfonic acid solution. Stir the mixture with a glass rod to insure an intimate mixing and then dilute to 500 ml. One ml. of this solution contains 0.01 mg. of nitrate nitrogen or 0.04427 mg. of nitrate. If the nitrogen is to be represented in terms of the nitrate radical use 0.1631 g. of pure potassium nitrate instead of the quantity described above. This standard contains 0.01 mg. of nitrate radical per ml. of solution.³⁴

Standard silver sulfate solution: Dissolve 4.397 g. of nitrate-free silver sulfate in 1 liter of water. One ml. of this solution is equivalent to 1 mg. of chloride.

Procedure. Measure into an evaporating dish a quantity of water to be analyzed that contains less than 1 mg. of nitrate nitrogen. One hundred ml. is usually sufficient, although a larger quantity should be used if the nitrate content is low. Determine the alkalinity, chloride and nitrite content, and the color of the sample. If nitrite nitrogen is present in a quantity greater than 1 p.p.m., it is removed by heating the sample for a few minutes with a few drops of nitrate-free hydrogen peroxide. The peroxide treatment should be repeated several times. Nitrite may also be removed by adding dilute potassium permanganate until a faint pink coloration persists. In this case the nitrogen equivalent of the oxidized nitrite must be subtracted from the final nitrate determination.

If the color of the sample exceeds 10 on the color scale, add 3 ml. of aluminum hydroxide and stir thoroughly, and then allow to stand for a few minutes. Filter and wash with distilled water and add sufficient 0.02 N sulfuric acid to neutralize the alkalinity to methyl orange.

If the chloride concentration exceeds 30 p.p.m. or 3 mg. in the portion of the sample used, add to the cold solution sufficient standard silver sulfate solution to remove all but about 0.1 mg. of chloride. Avoid an excess of silver sulfate, since most waters when heated with silver sulfate undergo an appre-

cial loss of nitrate nitrogen. Filter the treated solution and evaporate the filtrate to dryness. Add 2 ml. of phenoldisulfonic acid solution and stir with a glass rod to insure intimate contact. Dilute the mixture with distilled water and slowly add the potassium hydroxide solution until the maximum color is developed. A yellow color appears if nitrate is present. Transfer the solution to a Nessler tube, filtering if necessary, and compare the color with that of standards prepared as follows: add 2 ml. of potassium hydroxide solution to various volumes of standard nitrate solution and dilute to 50 ml. in Nessler tubes. The following volumes of standard nitrate solution may be used: 0.1, 0.3, 0.5, 0.7, 1.0, 3.5, 10, 20, 30, 40 and 50 ml. The standards so prepared contain from 0.001 to 0.5 mg. of nitrogen. These standards may be kept for several weeks without deterioration.

According to some investigators ammonium hydroxide is more satisfactory for neutralizing the reagent than potassium hydroxide. It is said that ammonium hydroxide develops a better color³⁵ and is less likely to yield a precipitate than potassium hydroxide.³⁴ The precipitate which forms is probably magnesium, and this may be prevented when potassium hydroxide is used by the addition of an ammonium salt.³⁸ Alekseeva and Gurvits^{11,12} recommend sodium hydroxide instead of ammonium hydroxide.

Color comparison may be made by balancing, dilution or duplication. According to Richardson and Hollings,³⁹ comparison with Lovibond glasses is also advantageous for a quick and approximate estimation of nitrates.

Since Chamot and co-workers²⁹⁻³¹ have described a method for the preparation of a reagent consisting of pure 1,2,4-phenoldisulfonic acid, tripotassium nitrophenoldisulfonate, which is available in a pure form, may be used as a standard. For use as a standard, dissolve 0.295 g. of the pure salt in water and dilute to 1 liter. This standard is used in the same manner as that described in the above procedure. If protected from light, it is stable for several years. To insure accuracy, compare a standard so prepared with standards prepared from pure potassium nitrate. Army and Ring⁴⁰ have found that permanent standards can be prepared from 0.5 N ferric chloride solution. A solution containing 66⅔ per cent of 0.5 N ferric chloride solution has exactly the same tint as that developed by a solution containing 1 part of nitrate nitrogen in 500,000 parts of solution. A 40 per cent 0.5 N ferric chloride solution corresponds to a nitrate nitrogen solution of 1 p.p.m. and a 20 per cent 0.5 N ferric chloride solution corresponds to a tint of 1 part in 2 million.

According to Stewart and Greaves,^{41,42} chlorides, either ionic or as some organic chloride, such as chloroform, cause low results in the determination of nitrate by phenoldisulfonic acid. When present in quantities greater than 2.6 p.p.m., the error due to chlorides is noticeable. The sulfuric acid of the reagent probably causes the formation of free hydrochloric acid, which reacts with nitric acid to form aqua regia. When present in quantities up to 30 p.p.m., however, chlorides cause an error not exceeding 10 per cent, and so in many determinations such as water analysis, it may not be necessary to remove chlorides.

Caron and Raquet⁴³ have studied the influence of chlorides on the determination of nitrates in water by means of phenoldisulfonic acid. They state that

the residue obtained by the evaporation of the sample should be cooled in a desiccator before addition of the reagent. When this precaution is taken, the amount of color change due to chloride is proportional to the amount of chloride present, and a correction may therefore be applied. In ordinary water containing 100 p.p.m. of chloride, interference may not be serious.

Several special procedures have been devised for determining nitrate in the presence of chlorides.⁴⁵⁻⁵² Gericke⁴⁵⁻⁴⁷ prevents loss of nitrate in the phenoldisulfonic acid method by adding 1.5 ml. of concentrated sulfuric acid and 2 ml. of the reagent to the aqueous solution to be analyzed, evaporating the greater part of the solution on a water bath, and then completing the evaporation to a volume of 6-14 ml. at a temperature not exceeding 70° C. Results with this method are excellent.

Johnson⁵³⁻⁵⁶ claims that a phenoldisulfonic acid reagent containing hydrochloric acid increases the sensitiveness of the nitrate test.

In general, chlorides are removed by treating with silver oxide or silver sulfate.⁵⁷⁻⁶⁵

Farcy^{66,67} has shown that bromides and iodides interfere with the nitrate determination by decolorizing the reaction product. This is probably due to the liberation of the free halogen acids, which form derivatives with the reagent. The ammonium salts of these compounds have no color.

Chamot and others²⁹ have shown that carbonates and organic matter, as well as chlorides, must be removed if accurate results are required. Carbonate corresponding to an alkalinity of 0.5 ml. of 0.1 N solution may be present, but with greater quantities results may be low.⁷⁰

Nitrites in quantities as low as 1 p.p.m. cause high results when nitrate is determined with phenoldisulfonic acid. Farcy⁴⁸⁻⁵⁰ has proposed a method for estimating nitrate with phenoldisulfonic acid in water containing nitrites and chlorides, and recommends a procedure for use with waters containing chlorides and ammonium salts.^{51,52}

According to Alekseeva^{11,12} standards should be treated with the same quantity of sulfate as contained in the unknown.

Sinnatt⁷¹ has determined nitrate by a titrimetric method which, according to him, is based upon the formation of picric acid, which is later titrated with titanous chloride according to the method of Knecht and Hibbert.⁷² Although it has been shown that picric acid is not formed in this reaction, Sinnatt claims that the method is more accurate than others based upon colorimetric principles.

One of the most important of the analytical applications of phenolsulfonic acid is in the determination of nitrates in water. The bibliography on this subject is very extensive.^{16-21,26-28,30,38,39,43,44,48-50,55-58,73-85}

Phenoldisulfonic acid has also been used extensively for the determination of nitrate in soil;^{9,10,36,37,86-97} in plant materials,⁹⁸⁻¹⁰¹ and in bismuth compounds.¹⁰² The reagent may also be used for the determination of the oxides of nitrogen in air,^{103-105,108} and sewage effluents.^{106,108}

Determination of potassium. Small quantities of potassium may be determined by an indirect method employing phenoldisulfonic acid. Potassium is

precipitated as the cobaltic nitrite, and, after filtration, the nitrogen of the precipitate is converted to nitrate and determined colorimetrically.^{109,110}

Procedure. Adjust the potassium concentration of the unknown to 0.05-2.0 mg. per ml. by evaporation or dilution as necessary. Transfer 1 ml. of this solution to a 25-ml. test tube and add 1 ml. of a freshly prepared 20 per cent solution of sodium cobaltic nitrite in 2 per cent sodium acetate. The unknown solution should be nearly neutral or only slightly acid, and should be adjusted to this range of acidity if necessary. Allow to stand 5-10 minutes after precipitation and filter through an asbestos pad. Wash with 70 per cent alcohol, and push the pad and precipitate into a 30-ml. test tube. Add 2 ml. of 40 per cent sodium hydroxide solution, and then add rapidly and with vigorous shaking 0.5 ml. of 50 per cent sulfuric acid. When all the precipitate has darkened, dilute to 25 ml. and filter.

Place 1 g. of chloroacetic acid in a dry test tube and add 0.5 ml. of the above filtrate, 1.2 ml. of 40 per cent sodium hydroxide and 0.5 ml. of 40 per cent sodium chlorate. Shake well and add 2.5 ml. of fuming sulfuric acid just rapidly enough to avoid excessive boiling. Again shake, blow out the fumes with a bent glass tube, and allow to cool. To the cool solution add 3 ml. of phenoldisulfonic acid. Shake well and add 20 ml. of water. Transfer to a 50-ml. volumetric flask and add a slight excess of 40 per cent sodium hydroxide solution. Dilute to volume and compare with a standard similarly and simultaneously prepared.

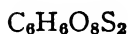
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PYROCATECHOLDISULFONIC ACID

Synonym: 1,2-Dihydroxybenzene-3,5-disulfonic acid



Mol. Wt. 270.23

Beil. Ref. XI, 297 (69).



Use: Detection and determination of iron.

Pyrocatecholdisulfonic acid is a crystalline solid which dissolves readily in alcohol and water.

Preparation: The sulfonic acid is prepared by warming 1 part of pyrocatechol with 5 parts of fuming sulfuric acid (30 per cent SO_3) at 100°C . for 30 minutes.^{1,2}

Detection and determination of iron. Sodium pyrocatecholdisulfonate reacts with ferric iron to form a highly colored and extremely stable complex. The complex is blue at a pH below 5, but is red above pH 7. One part of iron in 200,000,000 parts of solution can be detected by means of the red complex, while the blue complex is less sensitive and is capable of detecting only

1 part of iron in 30,000,000. The colors do not fade on standing even after several months.^{3,4}

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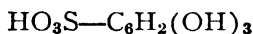
PYROGALLOLSULFONIC ACID

Synonym: 1,2,3-Trihydroxybenzene-4-sulfonic acid

$C_6H_6O_6S$

Mol. Wt. 206.17

Beil. Ref. XI, 310(73).



Use: Detection and determination of nitrate.

This compound consists of very hygroscopic crystals.

Preparation: Heat 5 g. of pyrogallol for a few minutes with 10 ml. of concentrated sulfuric acid at 80-90° C. Cool and dilute with water to 200 ml. A small quantity of sodium bisulfite may be added as a preservative.

Detection and determination of nitrate. Nitrates react with pyrogallol-sulfonic acid to give a pink color or a reddish-brown to olive green color. This reaction may be used to detect nitrates, and for the colorimetric determination of nitrates in soil.¹

Procedure. Agitate 10 g. of soil for an hour with 200 ml. of water, filter, and to 80 ml. of the filtrate add 1-3 ml. of saturated barium hydroxide solution. Boil, allow to settle, and add 0.5-1.0 ml. of 50 per cent lead subacetate solution. Allow to stand 2 to 3 minutes, and precipitate the excess barium and lead by adding 5 ml. of saturated sodium sulphate solution. Dilute to 100 ml., mix well, and filter. If nitrites are present, place 10 ml. of the solution in a porcelain dish and decompose with urea and 1 ml. of sulfuric acid. Let stand 10 minutes, add 0.5 ml. of pyrogallolsulfonic acid and mix with 20 ml. of concentrated sulfuric acid. Compare with standards similarly prepared.

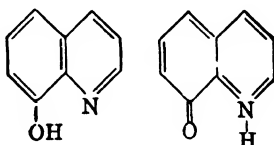
If the color is too strong, use pyrogallol as the reagent rather than pyrogallolsulfonic acid. As little as 0.0005 mg. of nitrate gives a pink color. With larger quantities of nitrate a reddish-brown or olive-green shade is obtained.

1. L. U. de Nardo, *Compt. rend.* 188, 563-5 (1929); *C.A.* 23, 2123 (1929).

CHAPTER XIII

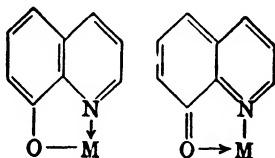
8-HYDROXYQUINOLINE AND ITS DERIVATIVES

8-Hydroxyquinoline and its derivatives, which are phenolic compounds, are of unusual importance in analytical chemistry. In these compounds the hydroxyl group is so located with respect to the nitrogen atom of the quinoline nucleus that 5-membered rings are formed with metals. Theoretically two structures are possible for the 8-hydroxyquinoline molecule:



Pure 8-hydroxyquinoline crystallizes in almost colorless crystals which dissolve in organic solvents. In the presence of water, however, the colorless solution changes to a yellow color. This is interpreted as being caused by the formation of the quinoid structure.

Metal ions react with 8-hydroxyquinoline to form inner-complex compounds in which the metal atom may be coordinatively bound either to the nitrogen atom or to the oxygen atom of the carbonyl group to form a stable 5-membered ring. These structures are shown by the following formulas.



in which M represents 1 equivalent of the metal. The many derivatives of 8-hydroxyquinoline which have been used as analytical reagents all contain the same reactive grouping as the parent compound, and so in general react similarly with solutions of metallic salts.

Many of the salts of 8-hydroxyquinoline are insoluble in various media and consequently are adaptable to the detection and determination of numerous cations. In order to increase the selectivity and sensitivity of these reactions, many derivatives of 8-hydroxyquinoline have been prepared and studied.¹⁻⁴ Among these are many azo derivatives which offer promise as analytical reagents.^{5,6,7} The dye formed by coupling diazotized *p*-nitroaniline with 8-hydroxyquinoline may be used as a precipitant for magnesium, nickel and cobalt.⁸

Boyd, Degering and Shreve⁵ have prepared and studied a number of other azo derivatives of 8-hydroxyquinoline, and have found that many of these com-

pounds give fairly sensitive tests for palladium and mercury. These compounds are listed on page 344.

1. J. Molland, *Compt. rend.* **210**, 144 (1940).
2. M. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934); *C.A.* **28**, 3683 (1934).
3. R. Berg, *Z. anorg. allgem. Chem.* **204**, 208 (1932).
4. J. Molland, *Arch. Math. Naturvidenskab.* **43**, 67-184 (1940).
5. T. Boyd, E. F. Degering and R. N. Shreve, *Ind. Eng. Chem., Anal. Ed.* **10**, 606-8 (1938); *C.A.* **32**, 8977 (1938).
6. P. Wenger, R. Duckert and D. Rieth, *Helv. Chim. Acta.* **25**, 406-15 (1942).
7. A. Gutzeit and R. Monnier, *Helv. Chim. Acta.* **16**, 478-85, 485-6 (1933); *C.A.* **27**, 3162-63 (1933).
8. C. E. Gietz and A. Sa, *Ann. Asoc. quim. Argentina.* **23**, 45-57 (1935).

8-HYDROXYQUINOLINE

Synonym: Oxine

C_9H_7ON

Mol. Wt. 145.15

Beil. Ref. XXI, 91.

Uses: Detection of aluminum, antimony, arsenic, beryllium, bismuth, cadmium, calcium, copper, gallium, magnesium, molybdenum, rhenium, thorium, tungsten, uranium, vanadium, zinc and zirconium.

Determination of aluminum, antimony, beryllium, bismuth, cadmium, cerium, chromium, cobalt, columbium, copper, gallium, germanium, indium, iron, lanthanum, lead, lithium, magnesium, manganese, molybdenum, nickel, phosphorus, rare earths, ruthenium, silicon, thorium, titanium, tungsten, uranium, vanadium, zinc and zirconium.

8-Hydroxyquinoline is a white crystalline compound. It melts at 74-76° C. and boils at 267° C. It is almost insoluble in water and ether, but is freely soluble in alcohol, acetone, chloroform, benzene and aqueous solutions of mineral acids.

The reagent is prepared by fusing quinoline sulfonic acid with sodium hydroxide:

Preparation: *Quinoline sulfonic acid:* Place a quantity of quinoline in a flask and add 10 times as much fuming sulfuric acid. Heat for about 8 hours on a water bath. The end of the reaction is indicated when a few drops of the liquid, after dilution with water, give no turbidity with sodium hydroxide. Pour the reaction mixture into a large quantity of water and add an excess of barium hydroxide. Filter off the yellow liquid. Boil the yellow precipitate with water, and combine the wash water with the filtrate. Concentrate the solution by heating, first over a free flame, and then on a water bath. Precipitate the excess barium hydroxide with carbonic acid, filter, and evaporate the filtrate to dryness. Dissolve the barium salt of the acid in boiling water, filter, and evaporate until crystals appear.

To prepare the free acid, dissolve the barium salt in water, or use the original solution of the barium salt, and carefully add sulfuric acid until all barium is precipitated. Filter, and concentrate the yellow acid filtrate strongly on a water bath until crystals of the acid appear on the surface of the liquid. Cool and collect the crystals, and wash several times with cold water, and then dissolve in the smallest possible quantity of hot water. The pure acid separates on cooling.^{7,815}

8-Hydroxyquinoline: Add the powdered quinoline sulfonic acid to 2-3 times its weight of sodium hydroxide to which has been added one fourth its weight of water, and then heat carefully over a free flame with stirring until the mixture is melted. At first the mass is greenish-yellow, and later the odor of quinoline is observed. At this point interrupt the heating to prevent further decomposition. Dissolve the melt in hydrochloric acid and decompose with sodium carbonate, and then pass steam through the mixture. 8-Hydroxyquinoline is volatilized and condenses in the receiver as colorless needles.⁸⁻¹¹

8-Hydroxyquinoline may also be prepared by the Skraup synthesis.

Preparation: Place 5 g. of *o*-nitrophenol, 8.3 g. of *o*-aminophenol (page 234) and 18 g. of glycerol in a 500-ml. flask and mix thoroughly. Add slowly, and with rotation of the flask, 8.2 ml. of concentrated sulfuric acid. Fit the flask with a reflux condenser and boil the liquid gently for 5 hours by heating in an oil bath. Remove any unchanged *o*-nitrophenol by distilling with steam, and add to the liquid remaining in the flask 12 g. of sodium hydroxide dissolved in water. Carefully add sodium carbonate until the liquid is alkaline and again steam distill. Keep the condenser so hot that uncondensed steam escapes from the outlet, which is inserted deep into the neck of a receiving flask which is cooled externally with a stream of water. Continue the distillation until 500-600 ml. of water have passed over. Cool the distillate, filter off the product and dry *in vacuo* or in air. The yield may be increased somewhat by extracting the filtrate with ether. Crystallize the product from warm alcohol by the careful addition of water, or from 70-90° ligroin, using 9 ml. of the solvent for each gram of solid.³¹⁴

Analytical Reactions of 8-Hydroxyquinoline. 8-Hydroxyquinoline was introduced as an analytical reagent by Hahn and by Berg^{1,2} in 1926-27, and it has since proved one of the most valuable organic analytical reagents discovered up to this time. It is very soluble in alcohol and acetic acid, and with many metals yields insoluble, and for the most part highly colored, inner-complex salts. These complexes have the general formula $M^{+n}(C_9H_6ON)_n$ (page 263). The hydroxyquinolates of molybdenum, thorium, titanium, tungsten and uranium do not correspond to the above formula. The formulas for these compounds are $MoO_2(C_9H_6ON)_2$, $Th(C_9H_6ON)_4 \cdot C_9H_6ON$, $TiO(C_9H_6ON)_2$, $WO_2(C_9H_6ON)_2$, $UO_2(C_9H_6ON)_2 \cdot C_9H_6ON$.

Many investigators have studied the use of 8-hydroxyquinoline as an analytical reagent, and they have developed many valuable separations and determinations. Generally, 8-hydroxyquinoline precipitates the same metals as ammonium hydroxide. These include magnesium, aluminum, iron, chromium, titanium, zinc, thorium, uranium, lanthanum, beryllium, vanadium, tungsten, molybdenum, gallium, indium, columbium, manganese, cobalt, bismuth, copper, cadmium and lead.

Despite the non-specificity of the reagent there are many very useful applications in analytical procedures. In many cases elements are completely precipitated at a definite pH but are soluble at other pH values. Thus, by a proper control of acidity, many important separations can be effectively carried out.

Goto^{3,4,5} has studied the importance of hydrogen ion concentration in the determination and separation of metals by means of 8-hydroxyquinoline. His results, combined with those of Fleck and Ward,^{60,178} are summarized in Table 37.

TABLE 37.—H-ION CONCENTRATION AND PRECIPITATION OF METALS

Metal	pH at Which Precipitation Begins	Range Through which Precipitation Is Complete
Aluminum	2.8	4.2-9.8
Antimony	>1.5
Bismuth	3.5	4.5-10.5
Cadmium	4.0	5.4-14.6
Calcium	6.1	9.2-13
Cerium (III)	Faintly basic
Chromium (III)	Slightly basic
Cobalt	2.8	4.2-11.6
Copper	2.2	5.3-14.6
Gallium	About 6-8
Indium	Acetic acid-sodium acetate
Iron (III)	2.4	2.8-11.2
Lead	4.8	8.4-12.3
Magnesium	6.7	9.4-12.7
Manganese	4.3	5.9-10
Molybdenum	3.6-7.3
Nickel	2.8	4.3-14.6
Palladium	Dilute HCl
Thorium	3.7	4.4-8.8
Titanium	3.5	4.8-8.6
Tungsten	5.0-5.7
Uranium	3.1	4.1-8.8
Vanadium	Acetic acid-sodium acetate
Zinc	2.8	4.6-13.4
Zirconium	Acetic acid-sodium acetate

* At a pH of 12-13, the precipitates of aluminum, nickel, manganese, titanium, uranyl, thorium and bismuth redissolve.

The metals may roughly be divided into three groups depending upon their precipitation characteristics in solutions of different pH ranges. These are:

(a) *The acetic acid-acetate group:* By varying the quantity of acetic acid and sodium acetate, the pH of a solution may be adjusted to any value between 2 and 6. In some procedures it may be advantageous to replace sodium acetate with ammonium acetate.

(b) *The ammonium hydroxide group:* The pH of a solution may be adjusted to any value between 6 and 10 by the use of ammonium hydroxide and tartaric acid or sodium tartrate.

(c) *The sodium hydroxide group:* Sodium hydroxide is used in place of ammonium hydroxide to obtain higher pH values.

The metals completely precipitated in acetic acid-acetate solutions are aluminum, gallium, indium, zinc, cadmium, mercury, copper, silver, nickel, palladium,

cobalt, iron, molybdenum, tungsten, uranium, columbium, tantalum, protoactinium, titanium, zirconium, hafnium, and thorium. Metals which are incompletely precipitated are scandium, yttrium, lanthanum, actinium, vanadium, chromium, manganese, ruthenium, rhodium, osmium, iridium, gold, thallium, tin and antimony.

Metals which are completely precipitated from ammoniacal solutions are beryllium, magnesium, scandium, yttrium, lanthanum, actinium, titanium, zirconium, hafnium, thorium, columbium, tantalum, protoactinium, uranium, manganese, iron, copper, zinc, cadmium, mercury, aluminum, gallium and indium. Those which are incompletely precipitated are calcium, strontium, barium, radium, vanadium, chromium, molybdenum and tungsten. Copper, magnesium, zinc and cadmium are completely precipitated in a sodium hydroxide solution.

TABLE 38.

Ion	HAc + NaAc	NH ₃ + tartrate	NaOH + tartrate	Ion	HAc + NaAc	NH ₃ + tartrate	NaOH + tartrate
Copper	—	+	+	Lead	+	+	—
Silver	+	—	—	Arsenious	—	—	—
Beryllium	—	+	—	Arsenic	—	—	—
Calcium	—	±	—	Antimonous ...	—	±	—
Strontium	—	±	—	Antimonic	—	—	—
Barium	—	±	—	Bismuth	+	+	±
Magnesium ...	—	+	+	Chromium	—	—	—
Zinc	+	+	+	Uranium	+	+	—
Cadmium	+	+	+	Manganese ...	+	+	±
Mercuric	+	+	±	Ferrous	+	+	+
Aluminum	+	+	—	Ferric	+	+	±
Titanium	+	+	—	Cobalt	+	+	±
Stannous	—	±	—	Nickel	+	+	±
Stannic	—	—	—				

Tables 38 and 39, prepared by Cattelain,⁶ summarize in a general way the precipitation characteristics of a number of common ions in acetic acid-sodium acetate, ammoniacal-tartrate, and alkali-tartrate solutions with 8-hydroxyquinoline. To illustrate the study of effect of pH on the precipitation of metals, the results of a series of determinations of zinc are reproduced in Table 40. A number of important separation procedures are based on the fact that many metallic ions are completely extracted from aqueous solutions by shaking with chloroform solutions of 8-hydroxyquinoline. The extraction of these ions from aqueous solutions as the hydroxyquinolates depends upon the pH of the solution. Thus, by carefully regulating the pH of the solution, various useful separations may be effected. Quantities of iron ranging up to 1 mg. in 25 ml. of aqueous

solution are completely extracted over a pH range of 1.9-3.0. A similar quantity of aluminum is extracted at pH 4.3-4.6; bismuth at 4.0-5.2; cobalt at 6.8 or above; nickel 6.7 and above; and copper 2.7-7.0. Calcium, magnesium and tungsten hydroxyquinolates alone of the common metals are insoluble in chloroform.

TABLE 39.—PRECIPITATION BEHAVIOR OF METALS WITH 8-HYDROXYQUINOLINE

Ion	Sodium Acetate 5 ml. Salt Soln. + 1 ml. Satd. NaAc		Ammonia 5 ml. Salt. Soln. + Few Drops Satd. Neutral Sodium Tartrate + Few Drops of NH_3		Sodium Hydroxide 5 ml. Salt Soln. + 0.5 ml. Satd. Neutral So- dium Tartrate + 0.5 ml. 2N NaOH	
	Mg. of Metal Precipitated	Sens.	Mg. of Metal Precipitated	Sens.	Mg. of Metal Precipitated	Sens.
Copper	0.008	1/30,000	0.012	1/410,000	0.018	1/270,000
Magnesium	0.016	1/312,000	0.024	1/200,000
Zinc	0.005	1/200,000	0.018	1/277,000	0.035	1/140,000
Cadmium ..	0.012	1/416,000	0.024	1/200,000	0.048	1/104,000
Aluminum ..	0.016	1/310,000	0.028	1/178,000		
Bismuth ..	0.017	1/300,000	0.023	1/217,000		
Uranium ..	0.021	1/239,000		
Manganese ..	0.014	1/357,000	0.029	1/172,000		
Ferric	0.013	1/384,000	0.021	1/238,000		
Cobalt	0.016	1/312,000				
Nickel	0.020	1/250,000				

TABLE 40. DETERMINATION OF ZINC

Acetic Acid ml.	Sodium Acetate g.	Sodium Tartrate g.	Ammonium Hydroxide ml.	Sodium Hydroxide ml.	pH	Error mg.
10 3N	2.84	No ppt.
10 3N	0.2	3.10	—9.87
10 3N	0.4	3.40	—2.63
10 3N	0.6	3.60	—1.67
10 3N	1.0	4.08	—0.15
5 1N	2.0	5.16	0.01
.....	...	1.0	6.18	0.10
.....	...	1.0	1.0	...	9.11	0.08
.....	...	2.0	...	5.0	12.96	0.05
.....	...	2.0	...	20.0	13.60	0.02

Methods of Determination. Metals may be determined gravimetrically, titrimetrically or colorimetrically after precipitation with 8-hydroxyquinoline. Although no general precipitation method can be devised which will be suitable for all precipitations, a number of helpful suggestions may be given.

1. An excess of the reagent is necessary for complete precipitation. An excess is indicated in an acetic acid solution by the appearance of a yellow color, and in an alkaline solution by an orange-yellow color. One disadvantage in using 8-hydroxyquinoline as a precipitant is its slight solubility in water, and to prevent precipitation of the reagent the excess used must be small. For this reason it is important to observe closely the color of the solution during precipitation.

8-Hydroxyquinoline is soluble in alcohol, acetone and acetic acid, and is generally dissolved in one of these solvents when used as a precipitant. A 2-4 per cent alcoholic solution is used for precipitating metals from alkaline solutions, and a 3-4 per cent 8-hydroxyquinoline acetate solution is used with acid solutions. When precipitation must be carried out in a neutral solution, an acetone solution of the reagent is recommended.

2. As a general rule solutions are heated to about 60-70° C. for about 5 minutes to facilitate crystallization and coagulation of the precipitate.

3. Frequently the filtrate obtained during filtration of the hydroxyquinolate becomes turbid. This is usually caused by the lower solubility of the reagent in cold solutions, but it may be caused by an insufficient quantity of 8-hydroxyquinoline. If the filtrate does not become clear on warming, more reagent should be added.

4. The precipitate is usually washed with hot water until the washings are colorless, but in some cases it is necessary to use special wash solutions.

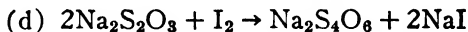
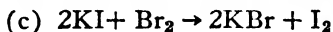
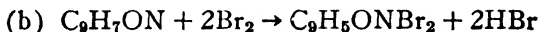
5. The excess 8-hydroxyquinoline is easily removed by adding ammonia to the filtrate and evaporating.

The precipitate of metal hydroxyquinolate may be treated in a variety of ways for the final determination of the metal. Gravimetric, titrimetric and colorimetric procedures have been used.

Gravimetric methods. The hydroxyquinolates generally have a definite composition, and may be weighed directly after drying at 105° C. In some instances the complex retains some water of hydration, and if the composition of the hydrate is unknown, or if the compound is unstable, the complex can be heated to 130-140° C. and weighed as the anhydrous compound. Sometimes it is preferable to mix the precipitate with oxalic acid and ignite to the metal oxide.

Titrimetric methods. A number of titrimetric methods for the determination of metals with 8-hydroxyquinoline have been proposed. 8-Hydroxyquinoline reacts readily and quantitatively with bromine, to form 5,7-dibromo-8-hydroxyquinoline. This reaction has been made the basis for a very useful method for determining metals after precipitation with 8-hydroxyquinoline. The hydroxyquinolate is dissolved in hydrochloric acid, treated with potassium bromide and an excess of standard potassium bromate solution. After adding potas-

sium iodide, the excess bromate is determined by titrating with standard thio-sulfate.^{98,213,216,298} The equations for the reactions are:



From the volume of bromate solution used, the quantity of metal may be calculated. The metals may be determined by precipitating with 8-hydroxyquinoline and determining the quantity of 8-hydroxyquinoline in the precipitate by titrating with a standard bromate-bromide solution.

Other methods are based on the quantitative oxidation of the organic portion of the hydroxyquinolate precipitates with standard permanganate or ceric salt solutions. Acidimetric methods are based on the fact that when a bivalent cation is precipitated with 8-hydroxyquinoline, 2 moles of acid are liberated, or with trivalent cations, 3 moles of acid are formed. The liberated acid is titrated by standard bases to give an indirect measure of the amount of metal precipitated.

Colorimetric methods. Most of the hydroxyquinolates are soluble in chloroform, forming strongly colored solutions. By extracting the complexes with chloroform, direct colorimetric comparisons are possible.²⁹⁰

Chloroform solutions containing up to 20 mg. of the hydroxyquinolates of iron, aluminum, bismuth, cobalt, nickel and copper per liter show little or no deviation from Beer's law and thus may be used for accurate colorimetric comparisons. Thus, copper can be determined in the presence of at least 40 times as much cadmium or zinc by extraction at pH 4.0 and measuring the transmittancy at 410 μ .

A number of metals, especially aluminum, gallium, indium and zinc, yield hydroxyquinolates which are strongly fluorescent in chloroform solution, and this property may be used for fluorometric determinations.

Indirect colorimetric methods have proved more generally useful than direct methods. Indirect methods are applied in a variety of ways after the hydroxyquinolate has been collected by filtration and washed free of excess reagent:

1. The hydroxyquinoline in the precipitate may be coupled to a diazo compound to form an intensely colored dye. The color of the dye is then compared with that of a standard similarly prepared.⁷⁶

2. 8-Hydroxyquinoline in a basic solution reduces phosphotungstic, molybdotungstic and phosphotungstomolybdic acids to form a blue solution which can be compared with a standard prepared in a similar manner.^{18,78}

3. A green color is obtained when certain hydroxyquinolate precipitates are dissolved in dilute acid and treated with ferric chloride solution. This color is suitable for a colorimetric comparison.^{16,20} This procedure may be modified by converting the precipitate to ferric hydroxyquinolate, which is filtered off and dissolved in alcohol. The resulting green-black color may be used for a colorimetric comparison.⁵³

4. Some metals such as magnesium can be determined indirectly by a colorimetric method which depends upon the fading of the color of a solution of 8-hydroxyquinoline when the metal is added and precipitated as the hydroxyquinolate. A part of the 8-hydroxyquinoline is removed in the formation of the hydroxyquinolate, and the amount is proportional to the amount of metal present.

Determination of Magnesium 8-Hydroxyquinoline forms a greenish-yellow, crystalline precipitate with magnesium ions from an ammoniacal solution, or from solutions containing sodium hydroxide and ammonium salts or neutral tartrates. Precipitation is complete over the pH range 9.4-12.7. This reaction is more sensitive than the usual precipitation as magnesium ammonium phosphate. In an ammoniacal solution, magnesium is precipitated by the reagent in the presence of potassium, sodium, lithium, calcium, strontium, and barium if certain precautions are taken. In sodium hydroxide solutions containing tartrate, the magnesium precipitate entrains copper, zinc, cadmium, and ferrous ions. The magnesium precipitate is very soluble in acids, and precipitation is prevented by the presence of acetic acid.²⁵⁰ With a proper control of conditions, precipitation of magnesium with 8-hydroxyquinoline is quantitative, although the composition of the precipitate depends somewhat upon its treatment after formation. A dihydrate of magnesium hydroxyquinolate ($\text{Mg}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$) is obtained when the magnesium precipitate is dried at a temperature of 105°C ., but if the drying is carried out at a temperature of $130\text{-}140^\circ\text{C}$., the anhydrous compound is formed. The compound can be weighed in either form, or it can be ignited to the oxide after the complex is destroyed by heating with anhydrous oxalic acid.

In addition to strictly gravimetric methods, magnesium can be estimated by titration of the hydroxyquinolate with bromine, potassium permanganate, or ceric salts; acidimetrically; or colorimetrically after treating with ferric chloride.

Gravimetric determination. Miller and McLennan¹² have studied various procedures for magnesium and recommend the following gravimetric method.

Procedure. To 100 ml. of solution to be analyzed, containing 10-50 mg. of dissolved MgO , add 2 g. ammonium chloride and 0.5 ml. of 0.02 per cent *o*-cresolphthalein in ethyl alcohol and 2 ml. of 6 N ammonium hydroxide in excess of the quantity required to make the solution neutral. Heat to 80°C . and slowly add a 1 per cent solution of 8-hydroxyquinoline in 2 N acetic acid until a slight excess is present as shown by the yellow color of the solution. Digest 10 minutes on a steam bath, filter, transfer the precipitate to a filtering crucible with the aid of the solution, wash with 50 ml. of hot water and dry at 105°C . for one hour, and then for half-hour periods to constant weight. The addition of very little sodium tauroglycolate prevents the precipitate from adhering strongly to the sides of the beaker. If the precipitate is slow in forming, allow to stand for 1 to 2 hours before filtering and stir mechanically for 15 minutes. The factor for magnesium is 0.0698. The factor for the anhydrous compound is 0.0778.

The composition of the magnesium hydroxyquinolate depends upon the manner in which it is formed, and upon the composition and conditions of the

solution. In general, contrary to the opinion of some, it appears preferable to add 8-hydroxyquinoline slowly with stirring to the magnesium solution which has previously been made alkaline with ammonium hydroxide (some prefer to add the reagent to an acetic acid solution of magnesium and then make alkaline). Drying at 105° C. also seems to be more satisfactory than the higher temperatures except when a considerable excess of reagent has been used, and in this case heating at 160° C. is better.

If a higher pH is necessary for certain separations, 2 N sodium hydroxide is substituted for ammonium hydroxide.

In general, sodium, potassium, lithium and ammonium salts do not interfere.²⁹²

The presence of ammonium oxalate retards the formation of the precipitate of magnesium hydroxyquinolate, and so when any considerable excess of the oxalate has been used for precipitating calcium, and particularly if the magnesium content is low, it is advisable to remove the ammonium salt by evaporation with nitric acid.

Titrimetric determination. A number of interesting and useful methods have been developed for the titrimetric determination of magnesium. These methods are based on the quantitative precipitation of magnesium with 8-hydroxyquinoline, and the determination by titration of the quantity of precipitant used or the amount of 8-hydroxyquinoline contained in the precipitate.

Bromate-bromide titration: Hahn¹³ has proposed the following modification of the Berg²⁹⁸ procedure which is based on determining the quantity of 8-hydroxyquinoline contained in the magnesium precipitate bromimetrically.

Reagents. *8-Hydroxyquinoline solution:* Dissolve 38 g. of 8-hydroxyquinoline in 125-130 ml. of 2 N hydrochloric acid and dilute to 1 liter.

Bromate-bromide solution: Dissolve 28 g. of potassium bromate and 50 g. of potassium bromide in water and dilute to 1 liter.

Procedure. To 20 ml. of solution containing 5-100 mg. of magnesium in a 250-ml. measuring flask, add 2-3 g. of ammonium chloride, 2-3 ml. concentrated ammonium hydroxide and 20 ml. of acetone. Heat gently on a water bath until near the boiling point, and add 8-hydroxyquinoline solution slowly from a buret until the resultant liquid has a yellow tint. Add more acetone if necessary to maintain a concentration about 50 per cent. If much reagent is necessary, heat frequently during the addition. Finally, add 10 ml. of acetone, dilute with water to about 200 ml. and allow the mixture to stand at least 1 hour. Make up to the mark, mix, and filter. Discard the first 50 ml. of filtrate and use the next 100 ml. for the analysis. Transfer to an evaporating dish, make acid to phenolphthalein with acetic acid, add 5 ml. of 5 per cent zinc sulfate solution, and evaporate for a half hour on a water bath. Pour into an Erlenmeyer flask, rinse the dish with 30 ml. of concentrated hydrochloric acid, and add an excess of the bromate-bromide solution. Finally, determine the excess bromate by adding potassium iodide and titrating with standard thiosulfate. One atom of magnesium reacts with 2 moles of 8-hydroxyquinoline, and is equivalent to two-thirds moles of bromate.

Values obtained with 5 mg. of magnesium agree to within 0.6 per cent. Fredholm²⁸ has proposed an improvement of Berg's method.

Following a study of the current methods for magnesium employing 8-hydroxyquinoline, Navez²⁴ reports that the titration method is the more rapid, but that it gives low results. The gravimetric method is so long, however, that the titration method is preferred unless extreme accuracy is desired.

Permanganate titration: Raskin and Drozd¹⁴ have applied the 8-hydroxyquinoline reaction to the determination of magnesium in blast furnace slags and silicates. Satisfactory results are obtained if not more than 2-4 mg. of MgO is present. The precipitate is not weighed, but determined by titration with potassium permanganate.

Procedure. Decompose 0.5 g. of the sample and separate silicon oxide, aluminum oxide, hematite, and calcium oxide in the usual manner. Dilute the filtrate to 500 ml. Add 2-3 drops of methyl red to 250 ml. of this solution, and add dropwise 15 per cent hydrochloric acid to a faint rose color. Add at 20-30° C. 8-10 ml. of 3 per cent 8-hydroxyquinoline solution. Shake 2-3 times and let stand 2-3 minutes. Introduce 5 ml. of ammonium hydroxide, shake, let stand 5-10 minutes, then boil for 1-2 minutes, and allow to stand for 30-40 minutes. Filter, rinse the flask with 5 per cent ammonium hydroxide and wash the precipitate with ammonium hydroxide until the wash solution remains perfectly colorless. Transfer the precipitate to a flask with hot, 10 per cent sulfuric acid, dilute the solution to 200 ml. with 10 per cent sulfuric acid, boil, and finally titrate with standard potassium permanganate. Calculate the results with the aid of the following equation:

$$\text{Per cent MgO} = N \times T \times 4 \times 0.0241$$

Where N is the number of ml. of potassium permanganate solution used, T the titer of the potassium permanganate and 0.0241 the factor for converting potassium permanganate to magnesium oxide. Results obtained with this method depend on the care with which the exact procedure is followed.

Cerate titration: Smith and Willard¹⁵ recommend 0.05 N ammonium hexanitratocerate in 2 M perchloric acid for the oxidation of the organic portion of magnesium hydroxyquinolate. They claim as advantages for the cerate oxidation, the elimination of bromination of the hydroxyquinolate, and the large cerate factor. One mole of magnesium requires 59.7 equivalents of the cerate as compared to the factor of 8 in the bromination procedure. The use of ceric sulfate has been studied,¹⁶ but this reagent has proved markedly inferior to the perchloratocerate in rate and extent of oxidation of 8-hydroxyquinoline.

Acidimetric titration: Hahn and Hartleb¹⁷ have suggested a somewhat different procedure for determining magnesium, zinc, aluminum and copper with the aid of 8-hydroxyquinoline. This method is based on the fact that when a bivalent cation is precipitated with the reagent, 2 moles of acid are liberated, or with trivalent cations 3 moles of acid are formed, and the liberated acid may be titrated using phenol red or α -naphtholphthalein as an indicator. From

the amount of acid set free, the quantity of the cation precipitated can be calculated.

Procedure. Neutralize any free acid present, using methyl orange as indicator. Then add an excess of 8-hydroxyquinoline and boil gently for 5-10 minutes. Add phenol red indicator and carefully titrate with 0.1 N sodium hydroxide until a red color is obtained. Immediately titrate with hydrochloric acid until the color is pure yellow, and then add 2-3 ml. of acid in excess. Heat 10-15 minutes to remove any base that was adsorbed by the precipitate, cool, and titrate with sodium hydroxide until a red color is obtained once again. One ml. of 0.1 N sodium hydroxide is equivalent to 1.2160 mg. of magnesium; 3.2828 mg. of zinc; 0.9007 mg. of aluminum; and 3.1783 mg. of copper.

Since the titration is not affected by barium, aluminum and zinc can be determined together in one sample, and in another sample zinc can be determined separately after precipitation of aluminum with a barium carbonate suspension.

The precipitates tend to entrain a little of the base and some indicator, but in some instances this difficulty can be eliminated by filtering or allowing the precipitate to settle, and then titrating an aliquot of the clear solution.

Carruthers²⁵⁹ has used a polarographic method for the microdetermination of magnesium. Magnesium is precipitated with 8-hydroxyquinoline, the precipitate is then dissolved, buffered and determined polarographically. From 68-100% of magnesium may be determined with an error ± 1.8 to ± 2.8 per cent. Stone³⁰⁷ has also used 8-hydroxyquinoline for the polarographic determination of magnesium.

Colorimetric determination. The indirect colorimetric determination of magnesium by means of 8-hydroxyquinoline can be carried out by various methods. These are usually applied after magnesium hydroxyquinolate has been collected by filtration and washed free of all excess reagent. The following methods have been described:

(a) Molybdotungstic acid, phosphotungstic acid and phosphotungstomolybdic acids are reduced by 8-hydroxyquinoline in an acid medium to yield a blue solution which can be compared with standards similarly prepared.^{18,78}

(b) The 8-hydroxyquinoline contained in the precipitate is coupled with a diazo compound to form a highly colored dye.⁷⁶

(c) The hydroxyquinolate is dissolved in dilute acid and treated with a solution of ferric chloride to give a green color,^{18,20,260} or the complex may be converted to ferric hydroxyquinolate, which is filtered off and dissolved in alcohol or other solvent to yield a green solution.^{53,289}

(d) Magnesium may also be determined colorimetrically by the decolorization of a yellow 8-hydroxyquinoline solution through precipitation of magnesium hydroxyquinolate.

Determination with phosphotungstomolybdic acid: Phenolic compounds react with phosphotungstomolybdic acid in the presence of an alkali to yield a deep blue color. The depth of the color produced is proportional to the concentration of the phenol. This reaction has been used by Berg¹⁸ and others^{293,294} for the determination of magnesium after precipitation with 8-hydroxyquinoline. This

method may be used for the determination of magnesium in blood when the calcium content is 40 times as great as that of magnesium. Sufficient reagent for the precipitation of calcium must be present. The 8-hydroxyquinoline reagent must be freshly prepared, since on standing it fails to give the magnesium complex and react with the phenol reagent.²⁹⁵ The reagents must not give the starch-iodide reaction.

The following method has been proposed by Berg and co-workers¹⁸ for the determination of magnesium in blood or serum:

Reagents. *Phosphotungstomolybdic acid reagent.* Dissolve 100 g. of sodium tungstate, 20 g. of phosphomolybdic acid and 50 ml. of 85 per cent phosphoric acid in 750 ml. of water and boil under reflux for 2 hours. Cool and dilute with water to 1 liter.

The reagent may also be prepared by the following procedure: Place 25 g. of molybdic oxide or 34 g. of ammonium molybdate in a large flask. Add 140 ml. of 10 per cent sodium hydroxide solution and 150 ml. of water. Boil for 20 minutes and add 100 g. of sodium tungstate, 50 ml. of 85 per cent phosphoric acid and 100 ml. of concentrated hydrochloric acid. Dilute to 750 ml. and boil under reflux for 4 hours. Add water from time to time to replace that lost by evaporation. Cool and dilute to 1 liter.

Standard magnesium solution. Dissolve 10 g. of ammonium chloride in 100 ml. of 1 per cent magnesium sulfate solution. Add concentrated ammonium hydroxide until the solution is just alkaline to phenolphthalein. Heat slowly to boiling and add 10 ml. of a 2 per cent alcoholic solution of 8-hydroxyquinoline. Boil for 10 minutes and filter on a Gooch crucible. Wash the precipitate with a hot 1:40 ammonium hydroxide solution until the washings come through colorless. Dry the precipitate at 100° C. Dissolve 0.1433 g. of the dry magnesium hydroxyquinolate in 20 ml. of 0.5 N hydrochloric acid and dilute with water to 500 ml. One ml. of this solution contains 0.01 mg. of magnesium.

Ammonium acetate wash solution. Add concentrated ammonium hydroxide to a 5 per cent solution of ammonium acetate until the mixture is alkaline to phenolphthalein.

Procedure. Place 1 ml. of oxalated blood or serum in a 15-ml. centrifuge tube and add 7 ml. of water. Mix and add 1 ml. of 10 per cent sodium tungstate solution and again mix. Add slowly and with stirring 1 ml. of 0.67 N sulfuric acid. Continue to stir vigorously for 10 minutes and centrifuge. Heat in a boiling water bath for 5 minutes while keeping covered to prevent evaporation. Transfer 5 ml. of the supernatant liquid to a 10 ml. centrifuge tube and add 0.5 g. of ammonium chloride. Mix and place in a water bath heated to 80° C. and slowly heat to boiling. Add 7 drops of 1:2 ammonium hydroxide and mix. Add 2 drops of a 2 per cent alcoholic solution of 8-hydroxyquinoline. Stir vigorously until the mixture becomes turbid and add 0.4 ml. of concentrated ammonium hydroxide. Mix well and heat for 10 minutes in boiling water. Decant and wash 3 times with 2 ml. of hot ammonium acetate wash solution. Decant and dissolve the precipitate in 1 ml. of 0.5 N hydrochloric acid.

Transfer this solution to a 25-ml. flask with a few ml. of water, and in a similar flask place 5 ml. of the standard magnesium solution. To each add 5 ml. of 20 per cent sodium carbonate solution and add 1 ml. of phosphotungstomolybdic acid reagent. Immerse the flasks in boiling water for 30 seconds and cool to room temperature. Dilute to the mark, mix well and compare.

Determination by conversion to a dye: A highly colored dye is formed by coupling 8-hydroxyquinoline with diazobenzene sulfonic acid. This reaction is used for the indirect determination of small quantities of magnesium: ¹⁹

Reagents. Mix 4 g. of 8-hydroxyquinoline with 8 ml. of glacial acetic acid and pour into 200 ml. of boiling water. Stir until dissolved and allow to cool.

Standard magnesium solution. Prepare as described in preceding method (page 275).

Sulfanilic acid solution. Dissolve 8.6 g. of sulfanilic acid in 1 liter of 30 per cent acetic acid.

Sodium nitrite solution. Dissolve 2.85 g. of sodium nitrite in 1 liter of water.

Procedure. Add 0.5 ml. of a saturated solution of sodium acetate to 1 ml. of the faintly acid solution of the unknown containing 0.01-0.5 mg. of magnesium. The sample should be free of ammonium salts and acidified with acetic acid. Add 0.5 ml. of the 8-hydroxyquinoline reagent and allow to stand 3 hours at room temperature to precipitate iron and aluminum. Add 4 drops of a saturated solution of ammonium oxalate to precipitate calcium, and warm on a water bath for 30 minutes.

Centrifuge if necessary and transfer the clear supernatant liquid to a clean tube. Wash the precipitate repeatedly with 0.5 ml. portions of cold water and add the washings to the main solution. Add 1 ml. of a saturated sodium tartrate solution to prevent precipitation of any remaining aluminum, and add 0.3 ml. of 8-hydroxyquinoline reagent. Make alkaline with 1 ml. of 2 N sodium hydroxide, and allow to stand overnight. Heat for 30 minutes on a water bath. Centrifuge, and remove the supernatant liquid from the magnesium hydroxyquinolate precipitate. Wash the precipitate with 2 ml. of hot 1:10 ammonium hydroxide, and repeat the washing.

Dissolve the washed precipitate in 2 ml. of hot N hydrochloric acid, and transfer the solution to a 50-ml. volumetric flask with the aid of 3 ml. of N hydrochloric acid. Dilute with water to about 30 ml. and add a mixture of 0.5 ml. of the sulfanilic acid solution and 0.5 ml. of the sodium nitrite solution. Mix well and let stand for 10 minutes. Add 10 ml. of 2 N sodium hydroxide solution, dilute to volume and mix well. Compare the resulting color with that of a standard similarly prepared from 1 ml. of standard magnesium solution. A standard prepared directly from an equivalent quantity of 8-hydroxyquinoline does not give satisfactory results.

Iron, aluminum, manganese, copper, zinc and titanium are precipitated with the reagent and must be removed as a preliminary to the magnesium determina-

tion. Calcium and barium are precipitated with ammonium oxalate. When iron, aluminum, calcium and phosphate are removed, the positive error of the method is 2-6 per cent.

Determination with feric chloride: Magnesium can be estimated colorimetrically by means of the green color which the hydroxyquinolate forms with ferric chloride.^{20,53,260}

Gerber, Claassen, and Boruff¹⁶ have studied this method and recommend the following procedure:

Procedure. Precipitate magnesium in the usual manner and dry the hydroxyquinolate in a gentle current of air. Add 10 ml. of 1 per cent acetic acid and warm in hot water until solution is complete, or about 5 minutes. Cool to room temperature and add 0.2 ml. of 3 per cent ferric chloride solution. Full color is developed within 5 minutes. Within the range of 5-100 γ , the solution obeys Beer's law.

Lavollay⁵³ has used a modification of this procedure.

Procedure. Precipitate magnesium as the hydroxyquinolate by the method described above and dissolve in hydrochloric acid (page 276). Transfer to a centrifuge tube. In another tube place 5 ml. of standard magnesium solution containing magnesium as the hydroxyquinolate (page 275). To each add 1 ml. of 10 per cent ammonium acetate solution and 0.5 ml. of 0.1 per cent ferric chloride solution. Mix well and add 3 drops of methyl red indicator solution. Add 0.25 N sodium hydroxide dropwise until the indicator changes color. Separate the precipitate of ferric hydroxyquinolate in the centrifuge, and wash both precipitates with water to remove the excess iron.

Dissolve the precipitates in 95 per cent ethyl alcohol containing a drop of ammonium hydroxide. Transfer the solutions to volumetric flasks and dilute to a volume which is suitable for comparison by balancing or dilution.

According to Sideris²¹ small quantities of magnesium can be determined colorimetrically by dissolving the insoluble hydroxyquinolate, formed in the usual manner, in hydrochloric acid and treating an aliquot part of the solution with ferric chloride. The greenish-black compound which is formed is extracted with chloroform, diluted with butyl alcohol, and compared with standards in a colorimeter. From 0.045 to 1.0 mg. of magnesium can be determined by this method with a maximum error of 10 per cent of the actual quantity of magnesium present.

Determination by decolorization of 8-hydroxyquinoline: Hough and Ficklen²² have determined very small quantities of magnesium by precipitating with a very carefully measured excess of 8-hydroxyquinoline, and then determining the excess by the color of the filtrate. The following method can be used for the determination of magnesium in water:

Reagent. Dissolve .5 g. of 8-hydroxyquinoline in 100 ml. of 95 per cent ethyl alcohol and dilute to 1 liter.

Procedure. To a sample having a volume not greater than 50 ml., add 20 ml. of 1:1 ammonium hydroxide and 50 ml. of 8-hydroxyquinoline reagent. Filter off the precipitate of magnesium hydroxyquinoline and wash on the filter with 20 ml. of 1:10 ammonium hydroxide. Dilute the filtrate to 100 ml. and compare with the 8-hydroxyquinoline solution diluted with an equal volume of water. The fading in color is proportional to the quantity of magnesium present. One ml. of the original 8-hydroxyquinoline solution is equivalent to 0.0416 mg. of magnesium.

This method gives results which are accurate to 10 per cent.

Volumetric Method. Hoagland²³ has determined magnesium in calcium-free blood and urine filtrates by measuring the volume of gas formed by the oxidation of magnesium hydroxyquinolate. Magnesium is precipitated with 8-hydroxyquinoline in the usual manner, and, after filtering and washing, the precipitate is oxidized with chromic acid to carbon dioxide. The gas is measured in a Van Slyke-Neill manometric apparatus. Aluminum, manganese, copper and zinc interfere, but this is not serious since these metals seldom occur in biological materials. Since the hydroxyquinolate contains 18 carbon atoms to each atom of magnesium, an accurate determination requires only 0.03 mg. of magnesium.

Other procedures have been suggested by Vucetich,²⁵ Carabelli,²⁶ Strebinger and Reif,²⁷ Miller,³⁰ and van der Marel.³¹

Special methods for determining magnesium in various materials are listed in Table 41.

TABLE 41.

Material to be Analyzed	Reference
Minerals and refractory stones	32, 288
Ferrous metals	33
Duralumin	34
Ferroaluminium alloys	35
Acid-soluble slags	36
Clays and chamotte	37
Brine from salt lakes	38
Aluminum alloys	39, 40, 41, 42, 43, 44, 45, 309
Blood serum and biological media	18, 20, 46, 47 48, 49, 50, 51, 52, 53
Carboate rocks and cement	54, 55, 296
Silicates	58, 59
Salts and medicinals	56, 57
Plants and soils	260

Separation of magnesium. The methods which have been proposed for separating magnesium from interfering metals are based upon two principles:

(a) Magnesium hydroxyquinolate is soluble in acids while the hydroxyquinolates of many other metals are quantitatively precipitated from buffered acetic acid solutions (page 266).

(b) Magnesium hydroxyquinolate is insoluble in chloroform while the hydroxyquinolates of most other metals are soluble. According to Sideris,²¹ magnesium can be separated from aluminum, iron, manganese, lead and zinc by precipitating the hydroxyquinolates of these metals in an ammoniacal solution, and extracting all except the magnesium compound with chloroform. The undissolved magnesium hydroxyquinolate is filtered off and determined according to the usual methods.

A number of the more important separations are described in the following sections:

Separation of magnesium and zinc. Magnesium and zinc may be separated by the following procedure:

Procedure. Add 5 g. of ammonium acetate and 2.5 ml. of glacial acetic acid to 80 ml. of the aqueous solution containing magnesium and zinc. Boil and add 10 ml. of 5 per cent 8-hydroxyquinoline solution in 2 N acetic acid. Filter off the zinc complex and precipitate magnesium in the filtrate by adding 30 ml. of 17.8 per cent sodium hydroxide solution.

Chirnside and co-workers⁶¹ claim that this separation can be effected only over a narrow pH range. According to Moyer and Remington⁶³ the separation is satisfactory if the pH is kept between 4.6 and 5.5. The separation of magnesium and zinc has also been studied by Hahn and Vieweg⁶⁵ and Cimermann and Wenger.⁶⁶

According to Fainberg and Fligel'man,⁶² magnesium can be precipitated with 8-hydroxyquinoline in the presence of zinc by adding to the solution to be analyzed sufficient potassium cyanide to form the complex zinc cyanide ion.

Magnesium and zinc may be separated by precipitating with 8-hydroxyquinoline in an ammoniacal solution and extracting the zinc hydroxyquinolate with chloroform. The magnesium compound is recovered by filtration.²¹

Separation of magnesium and copper. Copper, like zinc, can be separated from magnesium by forming the copper cyanide complex with potassium cyanide.⁶²

Separation of magnesium and nickel. Magnesium and nickel may be separated as follows:⁶⁰

Procedure. Add 5 g. of ammonium acetate and 5 ml. of glacial acetic acid to 80 ml. of solution containing magnesium and nickel. Boil and add 10 ml. of 5 per cent 8-hydroxyquinoline solution in 1 N acetic acid. Boil 5 minutes, filter off the complex nickel salt, and precipitate the magnesium in the filtrate by adding 30 ml. of 20 per cent sodium hydroxide solution.

Another method for separating magnesium and nickel is based on the conversion of the nickel ion to the cyanide complex with potassium cyanide before adding 8-hydroxyquinoline.⁶²

Separation of magnesium and alkalis. Magnesium may be separated from the alkali metals by precipitating with 8-hydroxyquinoline.^{65,292}

Separation of magnesium and iron. Magnesium can be separated from iron with the aid of 8-hydroxyquinoline but only over a narrow pH range.⁶¹ Magnesium and iron may be separated by first precipitating both metals from an ammoniacal solution with 8-hydroxyquinoline, and then extracting the iron compound with chloroform. Magnesium hydroxyquinolate is recovered by filtration.²¹

Separating magnesium and calcium. Wolff²⁰ states that magnesium can be separated from calcium by precipitation as the hydroxyquinolate at pH 8.2-8.5, and then treating the washed magnesium complex with 0.5 per cent acetic acid. Calcium hydroxyquinolate is slightly soluble in this medium.

Shead and Valla²⁸⁶ have used 8-hydroxyquinoline in a method for the separation and determination of calcium and magnesium. For the details of this procedure, see section on sucrose.

Unless calcium is present only in small quantity the more satisfactory procedure is to remove calcium as calcium oxalate, since calcium hydroxyquinolate is not very soluble and is likely to come down with the magnesium precipitate.

Separation of magnesium and alkaline earths. Magnesium and calcium may be precipitated quantitatively from a solution containing the alkaline earths by means of a saturated solution of 8-hydroxyquinoline in concentrated ammonium hydroxide. Under these conditions, very little barium or strontium is co-precipitated. If the precipitate is dissolved in dilute acetic acid, calcium can be precipitated as the oxalate; and, after filtration, magnesium can be precipitated as the hydroxyquinolate in the filtrate by the addition of ammonium hydroxide.^{67,250,296}

Separating of magnesium and bismuth. Bismuth is completely precipitated by 8-hydroxyquinoline at pH 5.2-5.4. After filtering, magnesium may be determined in the filtrate by making alkaline with ammonium hydroxide.³¹⁰

Separation of magnesium and manganese. The separation of manganese and magnesium is possible because magnesium does not form a precipitate with 8-hydroxyquinoline in an acetic acid solution. Manganese is precipitated from an acetic acid solution, and, after filtration, magnesium is precipitated by making the filtrate alkaline with ammonium hydroxide.⁶⁸ According to Smith,⁶⁹ 5-30 mg. of manganese can be separated from magnesium by a single precipitation with 8-hydroxyquinoline provided not more than 10 mg. of magnesium are present. With larger quantities of magnesium (0.1-0.5 g.) a double precipitation is necessary.

Manganese and magnesium may also be separated by precipitating with 8-hydroxyquinoline from an ammoniacal solution and extracting the manganese complex with chloroform. Magnesium is recovered by filtration.

Detection of magnesium. Gapchenko and Sheintzis⁷⁰ have used 8-hydroxyquinoline for the microdetection of magnesium. The addition of the reagent to a drop of a solution containing magnesium causes the formation of

a greenish-yellow amorphous precipitate. This soon changes to crystalline rosettes which can be identified microscopically. The sensitiveness of the reaction is 0.03-0.04 γ . In the presence of the alkali and alkaline earth metals the sensitiveness is as follows:

0.2 γ	Mg can be identified in the presence of	700 times as much K
0.2 γ	Mg can be identified in the presence of	500 times as much Ba
0.3 γ	Mg can be identified in the presence of	400 times as much Na
0.3 γ	Mg can be identified in the presence of	500 times as much Sr
0.4 γ	Mg can be identified in the presence of	200 times as much Ca

In the presence of heavy metals, except zinc, copper, and cadmium, the addition of alkaline sodium citrate prevents interference in the magnesium test.²⁵⁸

Determination of zinc. Zinc is quantitatively precipitated with 8-hydroxyquinoline as a greenish-yellow complex from acetic acid solutions which are buffered with sodium acetate. The pH range for complete precipitation is 4.6-13.4. When dried at 100° C. the precipitate has the composition $\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$. It becomes anhydrous when heated to 120-130° C. Zinc may be determined gravimetrically, titrimetrically, or colorimetrically by methods similar to those used with magnesium.

Zinc may be determined gravimetrically as follows:⁷¹

Procedure. To 100 ml. of a neutral solution containing 0.1 g. of zinc, add 2 grams of sodium acetate and 5 ml. of 10 per cent acetic acid. Heat to 60° C. and add 2 per cent alcoholic 8-hydroxyquinoline solution until the supernatant liquid is a canary-yellow color. Heat to boiling, and allow to stand 24 hours. Filter, and wash the precipitate with 40 ml. of water. Dry at 100° C. and weigh as $\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$. The factor for zinc is 0.1718. The precipitate may be weighed as the anhydrous compound after heating to 120-130° C. The factor for zinc in the anhydrous compound is 0.1850.

By the above procedure, zinc can be determined in the presence of aluminum, chromium, cobalt, nickel, lead, or the alkaline earths.

A more recent micromethod has been developed by Cimermann, Frank and Wenger.^{72,73}

Procedure. Treat the neutral solution containing 1-3 mg. of zinc with 1 drop of Merck's Universal indicator, 2 drops of 10 per cent acetic acid, and 6-7 drops of 40 per cent sodium acetate. The resulting solution has a pH of 5-6. Heat to boiling and add an excess (0.1 to 1.0 ml.) of freshly prepared 1 per cent alcoholic solution of 8-hydroxyquinoline. Stir, boil for 1-2 minutes, and filter through a filtering crucible. Wash the precipitate 8 times with water (1 to 2 ml.) and dry at 155-158° C. The factor for zinc is 0.1851.

Zinc hydroxyquinolate is reported to have a somewhat indefinite water content, and because of this a titrimetric method is recommended.

The above authors⁷⁴ have also determined zinc by a microtitrimetric method. This is based on bromination of the hydroxyquinolate with potassium bromate-potassium bromide according to the method of Berg^{98,213,216,298} (page 272). One ml. of 0.1 N potassium bromate is equivalent to 0.8172 mg. of zinc.

Karlson⁷⁵ has applied the method of Alten, Weiland, and Loofman⁷⁶ to the colorimetric determination of small amounts of zinc by coupling zinc hydroxyquinolate with diazotized sulfanilic acid in an alkaline solution. Zinc is estimated by comparing the resulting orange-rose dye with standard solutions similarly prepared, or by the use of a Pulfrich photometer.⁷⁷

Zinc may also be determined colorimetrically by the method of Teitelbaum⁷⁸ using Folin's reagent. The procedure is the same as that for aluminum (page 288). Good results are reported with 0.0081 to 0.083 mg. of zinc.

Zinc, like magnesium, can be estimated by titrating the acid liberated when zinc is precipitated with 8-hydroxyquinoline (see page 273).¹⁷ Zinc may also be determined polarographically after precipitation as the hydroxyquinolate.²⁸

Merritt³⁰² has described a rapid and accurate method for the determination of zinc by measuring the fluorescence of a turbidity of zinc hydroxyquinolate. From 0.05 to 0.60 mg. of zinc can be determined with an accuracy of 0.02 mg. Other ions which are precipitated by 8-hydroxyquinoline in acetic acid-acetate solutions interfere.

Minute quantities of zinc can be determined in organic substances by precipitation with 8-hydroxyquinoline, followed by decomposition of the precipitate with hydrochloric acid, and the determination of the resulting 8-hydroxyquinoline hydrochloride by its extinction coefficient.⁷⁹

Some effort has been made⁸⁰ to determine zinc by precipitation as the hydroxyquinolate, followed by the measurement of the volume of the precipitate after centrifuging, but this method is not very accurate.

The determination of zinc by precipitation with pyridine and ammonium thiocyanate, followed by reprecipitation with 8-hydroxyquinoline is reported to give poor results in the presence of large amounts of iron and aluminum.⁸¹ This is due to the solubility of Zn(Py)(CNS)_2 (Py = pyridine) in weakly acid solutions, and to its slow precipitation in an ammonium tartrate medium.

Zinc may be precipitated with 8-hydroxyquinoline in solutions containing 1 per cent acetic acid and 4 per cent sodium acetate in the presence of lead, provided the concentration of lead does not exceed 100 mg. per 50 ml.⁸²

Cimermann and Wenger⁸³ have used a microtitrimetric method for determining zinc, and various other investigators have studied methods for the separation and determination of this metal in the presence of other ions.^{60, 61, 65} A number of special methods for zinc have been proposed. These are listed in Table 42.

TABLE 42.

Material to be Analyzed	Reference
Soil	267
Metallic cadmium	84
Refined lead	85
Non-ferrous alloys	86
Aluminum and aluminum alloys	87
Plant materials	272

8-Hydroxyquinoline is also used for the recovery of zinc from plant materials as a concentration method for spectrographic analysis.²⁷²

Separation of zinc. By means of 8-hydroxyquinoline, zinc can be separated from ammonium, potassium, lithium, magnesium, calcium, strontium, barium, aluminum, chromium, lead, uranium, beryllium, manganese, iron, bismuth, mercury, arsenic, and antimony ions. It appears impossible, however, to separate zinc from cobalt or nickel.

Separation of zinc and manganese. A double precipitation with 8-hydroxyquinoline is necessary to separate completely zinc from manganese. About 2 mg. of zinc and not more than 5 mg. of manganese can be separated if the acidity is carefully controlled by buffering the solution from which precipitation takes place with acetic acid and sodium acetate.^{88,213}

Separation of zinc and ferric ion. Zinc and ferric iron can be separated by adding tartaric acid to the solution and neutralizing to bromthymol blue before precipitating with 8-hydroxyquinoline.⁸⁸

Separation of zinc and bismuth. In an alkaline tartrate solution, zinc can be precipitated in the presence of bismuth with 8-hydroxyquinoline.⁸⁸

Separation of zinc and mercury. Zinc can be separated from mercuric ions with 8-hydroxyquinoline if potassium cyanide is added to the solution before precipitation.⁸⁸ Zinc can be determined in the presence of mercury in an alkaline solution by masking the mercury with potassium cyanide and tartaric acid.⁷¹

Separation of zinc and arsenic or antimony. Pure precipitates of zinc hydroxyquinolate are obtained by adding 8-hydroxyquinoline to alkaline solutions containing zinc and arsenic or antimony.⁸⁸

Separation of zinc and beryllium. Beryllium and zinc can be separated in buffered acetate solutions by precipitating zinc with 8-hydroxyquinoline. This method is excellent when uranium is absent, but this metal precipitates with zinc.⁸⁹

Separation of zinc and uranium. Two methods have been described by Wiggins and Wood⁹⁰ for the determination of zinc in solutions containing uranium.

Procedure. Make the solution to be analyzed acid with acetic acid and add 25 per cent Rochelle salt solution until a faint turbidity of sodium uranate is produced. Add a few drops of acetic acid until the turbidity is cleared and heat. Add a 2 per cent solution of 8-hydroxyquinoline in alcohol, avoiding any considerable excess which will precipitate uranium. This is observed by the formation of a brown color.

A second method is carried out as follows: To the neutral solution to be analyzed, add 100 ml. of a solution prepared by dissolving 82 g. of malic acid and 49.5 g. of sodium hydroxide in sufficient water to make 1 liter of solution. Heat to 60° C. and add a 2 per cent alcoholic solution of the reagent until an excess is indicated by a dark green color. Cool and filter off the zinc precipitate.

Separation of zinc and alkali metals. 8-Hydroxyquinoline may be used for precipitating zinc in the presence of the alkali metals. The volume of the solution should be increased as a function of the concentration of the foreign salt present as follows:

5-20 ml. for 1-100 mg. alkali salt
10-20 ml. for 100-400 mg. of alkali salt
20 ml. for > 400 mg. of alkali salt

If the quantity of alkali salt is greater than 400 mg., the quantities of acetic acid and sodium acetate should be:

Acetic acid 1 ml. of 10 per cent acid
Sodium acetate 0.7 g.

These should be added to the neutral solution to be analyzed. After zinc is precipitated, the solution should stand 15 minutes, and during the last 5 minutes the mixture should be cooled in cold water.⁶⁴

Separation of zinc and alkaline earth metals. Zinc is precipitated from an acetic acid solution, while magnesium and the alkaline earth metals remain in solution. Ciemermann and Wenger^{64,65} have used this property of zinc for the separation of this metal from the alkaline earths.

Separation of zinc and magnesium. See separation of magnesium and zinc (page 279).

Separation of zinc and chromium. Zinc and chromium may be separated with 8-hydroxyquinoline if the concentration of the chromic ion does not exceed 10-12 mg.⁶⁴ Special conditions must be carefully observed.

Procedure. To a neutral or slightly acid solution containing 1-2 mg. of zinc and a maximum of 12 mg. of chromium as chromic ion, add dropwise a 4 per cent solution of sodium hydroxide until a slight opalescence appears. Add 2-3 drops of 10 per cent acetic acid to clear the solution, and then add 6 drops of 40 per cent sodium acetate solution and sufficient distilled water to make the total volume 5 ml. Heat just to boiling and add dropwise a large excess of a freshly prepared, 1 per cent alcoholic solution of 8-hydroxyquinoline. Shake and allow to stand 10 minutes. Cool the last 5 minutes in cold water. Filter through a glass filter (G3), wash, dry and weigh.

Separation of zinc and lead. Zinc and lead may be separated with 8-hydroxyquinoline if the quantity of lead does not exceed 30 mg. The precipitation is carried out in an acetic acid solution. The total volume of the solution should not exceed 20 ml. The precipitate should stand 1 hour before filtration, and should be filtered through a G4 filter, since the precipitate is very fine.^{64,68}

Detection of zinc. Zinc may be detected by the yellow precipitate which forms with 8-hydroxyquinoline.²⁸³ The reaction is very sensitive, giving a distinct test at a dilution of 1:1 million.² Tomsicek and Carney⁹¹ have used this reagent in place of hydrogen sulfide for the detection of zinc in the usual scheme

of qualitative analysis. Excellent results are claimed. 8-Hydroxyquinoline may also be used for the fluorescence analysis of zinc.²⁸⁸

Determination of cadmium. Cadmium is precipitated quantitatively with 8-hydroxyquinoline at pH 5.4 to 14.6 as $\text{Cd}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$.^{171,288} The greatest sensitivity for the cadmium precipitation is obtained with acetic acid solutions containing sodium acetate. As little as 0.012 mg. of cadmium in 5 ml. is precipitated. The sensitivity is 1:416,000.¹⁰⁴ This precipitate can be dried and weighed for the determination of cadmium.^{92,93} The precipitate obtained by air drying is the dihydrate, which contains 25.68 per cent cadmium. According to Berg,¹⁰⁴ the precipitate has the composition $\text{Cd}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ after drying at 100° C., although Fox²⁹¹ claims that the precipitate is anhydrous. Berg claims that the precipitate becomes anhydrous only after long heating at 120-130° C.

Cadmium may be determined by the following procedure:¹⁰⁴

Procedure. To a neutral or weakly acid solution containing cadmium, add sodium carbonate solution until a slight turbidity forms, and then add acetic acid until the solution is again clear. Warm and add 3-5 g. of sodium acetate, and then a slight excess of freshly prepared 2 per cent alcoholic or 4 per cent acetone solution of 8-hydroxyquinoline dropwise. The excess of reagent is noted by the yellow color of the supernatant solution. Heat just to the boiling point and filter through a glass filter crucible. Wash, first with warm, and then cold water and dry at 100-105° C. or 120-130° C. and weigh. The factor for the hydrate (100-105°) is 0.2629; for the anhydrous compound 0.2807.

The following micromethod is due to Wenger, Cimermann, and Wysze-wianska:⁹²

Procedure. To 2 ml. of neutral or faintly acid solution containing 1-3 mg. of cadmium in a microbeaker, add 1 drop of Merck's universal indicator, 1 drop of 3 per cent sodium carbonate solution, and 2-3 drops of 3 per cent acetic acid to dissolve any precipitate that forms with the sodium carbonate. Next add 6-10 drops of 40 per cent sodium acetate solution to make the pH 6-7 (shown by indicator). Heat to about 90° C. and add dropwise 3 times the theoretical quantity of 2 per cent alcoholic 8-hydroxyquinoline. Stir, heat to boiling, and allow the mixture to stand for 15 minutes. Filter, wash with hot water, and with two 1-ml. portions of cold water. Dry at 120-130° C. and weigh. The factor is 0.2807.

The greatest error observed in a series of measurements using this procedures was 0.007 mg. of cadmium with samples containing 1.5 mg. of the metal.

Wogrinz⁹⁴ has described a rapid method for determining the metal content of cadmium baths using 8-hydroxyquinoline.

Determination of aluminum. Aluminum is precipitated with 8-hydroxyquinoline from solutions buffered with acetic acid and sodium acetate or ammonium acetate, and from solutions containing a little acetic acid or tartaric

acid. Precipitation is quantitative at a pH range of 4.2-9.8. With the use of this reagent, aluminum can be determined gravimetrically, titrimetrically, or colorimetrically after coupling with suitable dyestuffs. The precipitates of aluminum hydroxyquinolate differs from the corresponding salts of copper, magnesium, zinc, and cadmium by being readily soluble in sodium hydroxide solutions.

Gravimetric determination. Many procedures for determining aluminum have been proposed.^{61,65,95-103,304} Typical of these is a gravimetric method proposed by Knowles.⁹⁹

Reagents. *8-Hydroxyquinoline solution:* Dissolve 12.5 g. of 8-hydroxyquinoline in 25 ml. of glacial acetic acid by warming gently. Pour this solution into 450 ml. of distilled water at 60° C., cool, filter, and dilute to 500 ml.

Bromocresol purple indicator: Dissolve 0.1 g. of the indicator in 18.5 ml. of 0.01 N sodium hydroxide and dilute to 250 ml. with distilled water.

Ammonium acetate buffer: Dissolve 30 g. of ammonium acetate in 75 ml. of water, and add 8-10 drops of the bromocresol purple indicator solution.

Procedure. To 200 ml. of sample, containing not more than 0.1 of aluminum and 10 ml. of hydrochloric acid, add 0.5 g. of tartaric acid (5 times the weight of aluminum to prevent precipitation during partial neutralization), 15 ml. of ammonium acetate buffer solution, and 13 per cent ammonia until a distinct purple color appears. The pH is approximately 6.8. Add rapidly the 8-hydroxyquinoline solution until all aluminum is precipitated, and then add 15-25 per cent in excess. Heat to boiling, cool to 60° C., and filter through a filtering crucible of fine porosity. Wash with 100 ml. of cool water, and dry at 135° C. Weigh as $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$. The factor for aluminum is 0.0587.

When more than 50 mg. of aluminum is present, results are high because of adsorbed reagent, whether the precipitate is weighed after drying or analyzed by bromination according to the method of Berg. In such cases it is advisable to dissolve the aluminum hydroxyquinolate in acid, destroy the organic matter by evaporation with sulfuric acid and nitric acid, and then determine aluminum by precipitation with ammonium hydroxide. If beryllium is present, determine aluminum as in the above procedure, but add the reagent slowly from a buret.⁹⁹

Titrimetric determination. Aluminum may be determined by titration after precipitation with 8-hydroxyquinoline by the following method:⁹⁹

Reagents. *Potassium bromate-potassium bromide solution:* Dissolve 27.835 g. of potassium bromate and 100 g. of potassium bromide in distilled water and dilute to 1 liter. Standardize against 0.1 N sodium thiosulfate solution.

Starch solution: Add 2 g. of finely powdered potato starch to 10 ml. of water, and then add 200 ml. of boiling water to this paste with constant stirring.

Procedure. Precipitate aluminum hydroxyquinolate as described above, and place the filtering crucible and its contents in a 600-ml. beaker containing 200 ml. of 10 per cent hydrochloric acid. Heat and remove the crucible, after

washing free of adhering liquid with 4 per cent hydrochloric acid. Dilute the resulting solution to 400 ml., cool to 17-23° C. and add a moderate excess of the bromate-bromide reagent. Add 5 g. of potassium iodide, allow the mixture to stand 5 minutes, and titrate the excess bromate-bromide reagent with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$, using starch as an indicator.

By the above procedure, 8-hydroxyquinoline is quantitatively brominated to 5,7-dibromo-8-hydroxyquinoline. One atom of aluminum is equivalent to 12 atoms of bromine, and 1 ml. of 0.1 N potassium bromate-potassium bromide solution is equivalent to 0.22475 mg. of aluminum.

An interesting method for determining iron, titanium, and aluminum in a mixture of the three metals has been suggested by Zan'ko and Bursuk.¹⁰⁶ The determination depends on the separation of iron with 8-hydroxyquinoline, and the precipitation of titanium and aluminum at different acidities with 5,7-dibromo-8-hydroxyquinoline. The latter is formed directly in the filtrate from the iron separation by bromination of the 8-hydroxyquinoline.

Procedure. To a solution containing 10 mg. of iron, titanium and aluminum, add 1 g. of tartaric acid and 3 g. of acetone. Neutralize with ammonium hydroxide and add 10 ml. of concentrated acetic acid and 6 ml. of 2 per cent 8-hydroxyquinoline in acetic acid. Digest the solution on a water bath for one-half hour, and filter off the iron precipitate through a Schott filter No. 4. Wash and dry at 110° C. to constant weight. The factor for iron is 0.1144.

Dilute the filtrate to 150 ml., and to 50 ml. of this solution add 20 ml. of 2 N hydrochloric acid and heat to 50° C. Then add 9 ml. of 0.2 N potassium bromate-potassium bromide solution and digest on a water bath 2-3 minutes. Filter off the titanium precipitate, wash with 200 ml. of 0.04 N hydrochloric acid containing 10 per cent acetone, and dry at 185° C. to constant weight. The factor for titanium is 0.0717.

To determine aluminum, concentrate if necessary the filtrate obtained after the separation of titanium and add 3 g. of ammonium nitrate and 15 ml. of acetone. Neutralize with ammonium hydroxide until the solution is slightly alkaline, and heat just to boiling. Then digest the mixture on a water bath for 10 minutes. Filter the aluminum precipitate through a Schott filter and wash, first with a warm 10 per cent acetone solution containing 1.5 per cent ammonium acetate and a little ammonium hydroxide, and then with water. Finally, dry at 190° C. to constant weight. The factor for aluminum is 0.0290.

When 1 mole of aluminum cation is precipitated with 8-hydroxyquinoline, 3 moles of acid are liberated, and by titrating the free acid, using phenol red or α -naphtholphthalein as indicator, the quantity of aluminum precipitated can be indirectly estimated.¹⁷ The method used is similar to that for magnesium (page 273). Aluminum may be determined polarographically after precipitating as the hydroxyquinolate.²⁶¹

According to Navez²⁴ a comparison of the gravimetric and titration methods for aluminum indicates that the latter is preferred, although less accurate, because of the time required for a complete gravimetric determination.

Colorimetric determination. Alten, Weiland, and Loofman⁷⁶ and Haendler and Thompson¹¹¹ have proposed satisfactory methods for the colorimetric determination of aluminum.

Reagents. *8-Hydroxyquinoline solution:* Dissolve 0.3226 g. of 8-hydroxyquinoline in 10 ml. of glacial acetic acid and dilute to 1 liter with distilled water. One ml. of this reagent reacts with 20 mg. of aluminum.

Sulfanilic acid solution: Dissolve 8.6 g. of sulfanilic acid in 1 liter of 30 per cent acetic acid.

Sodium nitrite solution: Dissolve 2.85 g. of sodium nitrite in 1 liter of distilled water.

Procedure. Place 2-5 ml. of an acid solution containing 0.03-0.5 mg. of aluminum in a centrifuge tube, and add a few crystals of ammonium sulfate. If calcium or magnesium is present, add 1 ml. of 30 per cent hexamethylenetetramine solution, and heat to boiling. Centrifuge at 2000 r.p.m. for 3 minutes, and carefully remove the supernatant liquid with a capillary tube. Add 2 ml. of water to the residue, again centrifuge, and remove the water with a capillary tube. To the precipitate of aluminum and iron, if the latter is present, add 1 ml. of 0.5 N sodium hydroxide and 1 ml. of water, and heat to boiling. Centrifuge, and remove the supernatant liquid containing sodium aluminate with a capillary tube. Wash the residue twice with 1-ml. portions of water by heating, centrifuging, and removing the supernatant liquid.

Acidify the solution containing aluminum with 2 drops of glacial acetic acid, then add 0.6 ml. of a saturated solution of sodium acetate and 1 ml. of 8-hydroxyquinoline solution. Heat to 70° C. for 30 minutes and centrifuge. Decant the supernatant liquid, wash the residue with two 1-ml. portions of water, and remove the wash water by decantation. To the precipitate add 2 ml. of a mixture prepared by diluting 2 N hydrochloric acid with an equal volume of ethyl alcohol, heat to dissolve the precipitate, and then dilute to 50 ml. with distilled water. To an aliquot part of this solution, containing about 0.05 mg. of aluminum, add 0.5 ml. of sulfanilic acid reagent and 0.5 ml. of sodium nitrite solution. Mix thoroughly, allow to stand 10 minutes, add 10 ml. of 2 N sodium hydroxide, dilute to 50 ml., allow to stand 10 minutes, and compare the resulting deep yellow-red color of the solution with standards prepared similarly.

The accuracy of this method is about 96 per cent. Iron causes a darker color and calcium and magnesium cause low results. This method is recommended for use with absolute methods of measurement of color. Errors as high as 20 per cent may occur with only 0.01 mg. of aluminum. As little as 0.02 mg. of aluminum is sufficient for the development of the color with sodium hydroxide by the above method. The color obeys Beer's law, is stable 4 hours, and is easily compared with a blank.

Aluminum may also be determined colorimetrically according to the method of Teitelbaum.⁷⁸

Folin's reagent. Place 25 g. of molybdic oxide or 34 g. of ammonium molybdate in a large flask and add 140 ml. of 10 per cent sodium hydroxide

solution and 150 ml. of water. Boil for 20 minutes and add 100 g. of sodium tungstate, 50 ml. of 85 per cent phosphoric acid and 100 ml. of concentrated hydrochloric acid. Dilute the mixture to 700-800 ml. and close the mouth of the flask with a funnel and watch glass. Boil gently for 4 hours, adding water from time to time to replace the water lost by evaporation. Cool and dilute to 1 liter.

Procedure. Adjust the acidity of 1-4 ml. of the sample solution to about pH 3.0. Add 0.5 ml. of saturated sodium acetate solution and 4 drops of 0.5 per cent solution of 8-hydroxyquinoline acetate. Heat on a water bath for 15 minutes, cool, and dilute to 5 ml. Centrifuge for 10 minutes at 2000-2500 r.p.m. and decant the clear liquid. Mix the precipitate with 5 ml. of water and again centrifuge. Repeat the washing with 2 ml. of water.

Dissolve the precipitate in 1 ml. of 1:2 hydrochloric acid and transfer to a 25-ml. volumetric flask with 15 ml. of water. Add 1 ml. of Folin's reagent and 6 ml. of a cold saturated solution of sodium carbonate. Dilute to the mark, allow to stand for 30 minutes, and compare with standards similarly and simultaneously prepared. Excellent results are obtained with 0.0018-0.32 mg. of aluminum.

TABLE 43.

Material	Reference
Minerals	288
Beryllium minerals	110, 129,
Sea water	111
Portland cement	112
Magnesium alloys	113, 285
Clay, kaolin, feldspar	114, 118,
Silicates, and soil	115, 122, 126, 132,
Steel	116, 119, 133, 135,
Ferrous alloys	117
Zinc and zinc alloys	120
Ores, grog, and clay	121, 130,
Nitriding steels	123
Slag obtained by the electrolysis of steel	124
Soil solutions	125
Aluminum protein compounds	127
Tungstic acid	128
Preserves	131
Iron ores and slags	134
Aluminum ores	136
Corundum	137
Feldspar	138
Copper, nickel, aluminum alloys	139, 263, 308
Plants	264
Spelter	311
Nickel-chromium steels	306
Titanium pigments	312

Special applications. Nakamura and Yamazaki¹⁰⁶ have determined aluminum oxide in aluminum using 8-hydroxyquinoline. Aluminum oxide may also be determined in steel by a similar method.²⁶⁵ Aluminum may also be determined in cryolite¹⁰⁷ with excellent results by the fixation of fluoride with a large excess of boric acid (30 parts of boric acid to 1 part of fluoride) and back titration of the excess of the 8-hydroxyquinoline used for the precipitation by the method of Zhukovskaya and Balyuk.¹³⁰ Aluminum may be determined in the presence of phosphoric acid by the method of Balanescu and Motzoc.^{108,109} A number of methods for determining aluminum in special materials are listed in Table 43.

Separation of aluminum. Aluminum can be separated from beryllium, phosphorus, arsenic, fluorine, boron, vanadium, columbium, tantalum, titanium, molybdenum, iron, magnesium, cobalt, nickel, copper, chromium, lithium, the alkali metals, and the alkaline earths with the aid of 8-hydroxyquinoline.

Separation of aluminum and beryllium. Aluminum may be separated quantitatively from beryllium by precipitating aluminum as the hydroxyquinolate in a dilute acetic acid solution. Beryllium remains in the solution.^{99,140-146} The following method is described by Lundell and Knowles:¹⁴⁰

Reagent. Add 2.5 g. of 8-hydroxyquinoline to 5 ml. of glacial acetic acid and pour the resulting solution into 100 ml. of water at 60° C. Cool and filter. One ml. of this solution will precipitate 2.9 mg. of alumina in a pure solution.

Procedure. Make the solution to be analyzed slightly acid with acetic acid and warm to 50-60° C., and add a slight excess of the 8-hydroxyquinoline solution. Add 2 N ammonium acetate until a permanent precipitate is formed, and then add 25 ml. in excess. Allow the mixture to stand and filter through a Jena glass, or a porous porcelain crucible. Wash with cold water, and dry at 120-140° C. Beryllium in the filtrate may be determined by precipitating with ammonia and igniting the residue to the oxide. The factor for aluminum is 0.0587.

Hackl¹⁴⁷ has studied the separation of beryllium and aluminum with 8-hydroxyquinoline, and has found that if chromium, either as chromic salts or as chromates, is present, it too is more or less completely precipitated.

Separation of aluminum from phosphorus, arsenic, fluorine, and boron. Lundell and Knowles¹⁴⁰ have studied the separation of aluminum from phosphorus, arsenic, fluorine, and boron, and recommend the following procedure:

Reagent. Use same reagent as described under the separation of aluminum and beryllium (page 290).

Procedure. Make the solution to be analyzed, containing not more than 0.1 g. of aluminum oxide in 100 ml. of solution, slightly acid with hydrochloric or sulfuric acid and add an excess of the 8-hydroxyquinoline reagent. Next add dilute ammonium hydroxide until the solution is alkaline, and finally add an excess of 5 ml. of concentrated ammonium hydroxide in 100 ml. of

solution. Warm to 60-70° C. and allow the mixture to stand at this temperature until the precipitate is dense and crystalline. Cool, preferably in ice water, and filter through tight paper. Wash the precipitate thoroughly with a cold 1:40 solution of ammonium hydroxide containing 25 ml. of the reagent (previously neutralized with ammonium hydroxide) in 1 liter. Treat the precipitate and filter paper with nitric and sulfuric acids to destroy the organic matter, and then precipitate aluminum with ammonium hydroxide, and finally ignite to the oxide. Correct for silica.

Separation of aluminum from vanadium, tantalum, columbium, titanium, and molybdenum. Aluminum is separated from vanadium, tantalum, columbium, titanium, and molybdenum by essentially the same procedure as that used for separating aluminum from phosphorus, arsenic, fluorine, and boron, except that 10-15 ml. of 3 per cent hydrogen peroxide is added before precipitation with 8-hydroxyquinoline (see above procedure).¹⁴⁰

Separation of aluminum from iron, cobalt, nickel, copper, molybdenum and chromium. Aluminum can be separated from iron, cobalt, nickel, copper, molybdenum and chromium by precipitating with 8-hydroxyquinoline. Treat the acid solution with tartaric acid, and add ammonia and potassium cyanide (caution).¹⁴⁹ In the presence of iron, treatment with potassium cyanide does not serve to form complex compounds unless hydrogen sulfide is introduced after the addition of the potassium cyanide. If much chromium is present, it is best to convert it to the chromate ion by treatment with silver ion and persulfate. In place of the 8-hydroxyquinoline reagent in acetic acid, it is necessary to use a 10 per cent solution in alcohol.

Ferrous ions can be masked with potassium cyanide and aluminum determined in an ammoniacal solution.²⁹⁷

Separation and determination of iron, titanium, and aluminum in a mixture. Zan'ko and Butenko¹⁴⁸ have improved the method of Tzinberg³⁵ and its modification by Zhukovskaya and Balyuk²⁵⁷ for the determination of aluminum. This improvement is based on an accurate control of the acidity of the solution from which precipitation is carried out, and a definite balance between the concentration of tartaric acid and ammonium oxalate, thus making possible a complete separation of titanium and aluminum with the aid of 8-hydroxyquinoline. Iron, titanium, and aluminum may be determined in a mixture of the three by the following procedure:

Procedure. To 100 ml. of the solution to be analyzed, add 3 g. of ammonium acetate and 1 g. of tartaric acid. Neutralize with ammonium hydroxide, and add 20 ml. of 80 per cent acetic acid, and a slight excess of 2 per cent 8-hydroxyquinoline acetate. Heat almost to boiling, digest for a time on a water bath, and filter off iron hydroxyquinolate through a glass filter No. 4. Wash the precipitate with 1 per cent acetic acid and water, dry at 110° C., and weigh. The factor for iron is 0.1144.

Evaporate the filtrate to about 150 ml. and add 4 g. of ammonium oxalate. Neutralize with ammonium hydroxide to litmus, and add 3-5 drops of acetic

acid. Heat to 60° C. and precipitate with 8-hydroxyquinoline acetate. Boil for 10 minutes, filter off the precipitate of titanium hydroxyquinolate, wash with hot water, dry at 110° C., and weigh. The factor for titanium is 0.1361.

Dilute the filtrate to 500 ml., and to a 100-ml. aliquot add an excess of ammonium hydroxide and 8-hydroxyquinoline acetate, and proceed with the separation and determination of aluminum in the usual manner. The factor for aluminum is 0.0587.

Separation of aluminum and iron. Aluminum can be separated from iron with 8-hydroxyquinoline only if the acidity is kept within the narrow limits of pH 3.5-4.0.^{63,148}

Determination of indium. Indium can be determined satisfactorily with 8-hydroxyquinoline in an acetic acid solution buffered with sodium acetate. The procedure of Geilmann and Wrigge¹⁵⁰ is carried out as follows:

Procedure. To the solution containing 15-100 mg. of indium, add 2 g. of sodium acetate and 2 ml. of acetic acid. Dilute to 200 ml. with hot water, heat to 70-80° C., and add an alcoholic solution of the reagent. Wash the precipitate into a filtering crucible and wash, first with hot water, and then with cold water. Dry at 120° C. and weigh as $\text{In}(\text{C}_9\text{H}_6\text{ON})_3$. The factor for indium is 0.2098. To recover indium from the precipitate, digest with nitric and sulfuric acids and dilute with water, and finally precipitate with ammonium hydroxide.

Royer¹⁵¹ has used the following micromethod:

Reagent. Dissolve 5 g. of 8-hydroxyquinoline in 12 g. of acetic acid and 83 ml. of water.

Procedure. Make the solution to be analyzed slightly acid with a drop of concentrated hydrochloric acid, add 5 ml. of reagent, and warm on a steam bath. When the mixture is warm, add 2 N ammonium acetate dropwise until the solution becomes turbid. After about 1 minute, the precipitate becomes crystalline. Then add an additional 0.5 ml. of ammonium acetate solution. Digest the precipitate for a time, filter, wash with hot water, dry, and weigh.

The average deviation of a series of determinations using this method was ± 1.2 per cent. The indium ion can be extracted completely from aqueous solutions of pH 3.2-4.5 by shaking with a chloroform solution of 8-hydroxyquinoline.²⁷⁵ Indium hydroxyquinolate dissolves readily in chloroform to yield a yellow solution which may be used for the colorimetric determination of small quantities of indium. The yellow chloroform solutions obey Beer's law in concentrations ranging up to 18 mg. of indium per liter of chloroform. At pH 3.5 the following metals interfere by giving a colored chloroform extract: aluminum, gallium, trivalent thallium, bivalent tin, bismuth, copper, trivalent iron, pentavalent vanadium, hexavalent molybdenum, nickel and cobalt. Magnesium, calcium, strontium, zinc, cadmium, bivalent mercury, tetravalent tin, lead, manganese, silver and trivalent chromium are not extracted at this pH.

Indium can be estimated accurately in the presence of considerable quantities of zinc, cadmium and lead ions. It appears impossible to determine indium

accurately in ferric-indium solutions by extraction of iron at low pH, and the subsequent extraction of indium, followed by a colorimetric comparison.

Procedure. Adjust the pH of a 25-ml. portion of the aqueous solution of the indium salt to 3.5 and extract with five successive 5-ml. portions of a 0.01 M solution of 8-hydroxyquinoline in chloroform. Dilute the combined extracts to 50 ml. with chloroform and examine colorimetrically. This procedure yields results accurate for indium concentrations ranging from 0.3 to 20 mg. per liter of chloroform or 0.015-1.00 mg. of the metal in 25 ml. of the aqueous solution.

Chloroform solutions of indium hydroxyquinolate fluoresce strongly, and thus small quantities of indium may be determined fluorimetrically. The method is similar to that for gallium.

Detection and determination of gallium. Gallium can be determined gravimetrically as $\text{Ga}(\text{C}_9\text{H}_6\text{ON})_3$ by a method similar to that employed for indium. The procedures are similar except that for the determination of gallium the solution is neutral or made slightly alkaline with ammonium hydroxide rather than acidified with acetic acid. The pH should be 6-8, excellent results are claimed.¹⁵⁰

Gallium can be separated from vanadium and tungsten by precipitating from an ammoniacal solution by means of 8-hydroxyquinoline. After filtration from gallium hydroxyquinolate, vanadium can be determined in the filtrate by very carefully neutralizing with acetic acid and boiling with 1 ml. of saturated ammonium carbonate solution until the mixture is neutral to litmus. The precipitate is dissolved in 2 N sulfuric acid and vanadium precipitated with cupferron.¹⁵² Gallium and tungsten are separated similarly.¹⁵²

Gallium is often detected by methods employing alizarin, quinalizarin, and morin after it is first separated from interfering substances with the aid of 8-hydroxyquinoline. The precipitate of the hydroxyquinolate is dissolved in hydrochloric acid and spot tests are made with this solution.¹⁵³ Wenger and Duckert,¹⁵⁴ however, after a careful study of gallium reagents, claim that 8-hydroxyquinoline, as a precipitate for gallium, is not sufficiently sensitive.

Gallium hydroxyquinolate can be extracted from an aqueous solution at pH 2.6-3.0 by shaking with chloroform. The chloroform solution exhibits a strong yellow fluorescence in ultra-violet light. This reaction has been used by Sandell¹⁵⁵ as a sensitive test for gallium.

Reagent. Warm 0.10 g. of pure 8-hydroxyquinoline with 1 ml. of 4 N acetic acid until the solid is dissolved and dilute to 100 ml. with water.

Procedure. Adjust the pH of 5-10 ml. of solution to be tested to 2.5-2.6 (if more than 0.05 mg. of indium is present, otherwise make the pH 3.0) and add 0.25 ml. of 0.1 per cent 8-hydroxyquinoline in acetic acid. Mix well, add 1 ml. of chloroform, shake and let stand until clear. View the layer transversely while the tube is held in a vertical position above a source of ultraviolet light (Westinghouse G-5) in a dark room. As little as 0.1 γ of gallium can be detected in 5-10 ml. of solution by this method.

Ferric iron interferes, and must be reduced by the addition of 0.5 g. of hydroxylamine hydrochloride, followed by the addition of sodium acetate until a brown color appears. This solution is treated as above after adjusting the pH to the proper value. Vanadate is reduced in a similar manner. Copper is precipitated and removed as insoluble copper thiocyanate, and molybdenum is precipitated with lead nitrate in an acetic acid solution. This test is particularly suitable for the detection of gallium in the presence of large quantities of iron and aluminum.

Aluminum hydroxyquinolate is not extracted under the conditions of the test. Indium reacts slightly at pH 3.0 and is partially extracted to impart a fluorescence to the chloroform solution. At a pH of 2.6, however, 1 mg. of indium in 5 ml. of aqueous solution gives only a slight, if any, fluorescence to 1 ml. of chloroform. Bivalent copper, pentavalent vanadium and hexavalent molybdenum interfere by reacting with 8-hydroxyquinoline to form extractable complexes at pH 2.6-3.0. This causes a weakening of the fluorescence of gallium. The chloroform solution of these metallic hydroxyquinolates, however, does not fluoresce. Large quantities of lithium cause a slight fluorescence, as do beryllium and scandium. Zinc weakens the fluorescence, and fluoride similarly interferes unless aluminum is present. Citrate inhibits the reaction, but phosphate has only a slight effect.

The reaction between gallium and 8-hydroxyquinoline has not been extensively studied as a quantitative colorimetric procedure, but results indicate that the method is suitable for determining gallium in the presence of aluminum and iron if the latter is in the ferrous state. The quantitative procedure is carried out exactly as described for the gallium test, except that the fluorescence is compared with standards. The comparison is made in 1.8×15 cm. glass-stoppered flat-bottomed tubes. Standards are prepared from solutions of known gallium content, having the same volume and pH as the unknown solution, and having as nearly as possible the same composition as regards neutral salts. The comparison may also be made by a fluorometric titration.²⁰⁰ Results are shown in Table 44.

TABLE 44.—DETERMINATION OF GALLIUM WITH 8-HYDROXYQUINOLINE

Foreign Elements	Gallium Present γ	Gallium Found γ
Aluminum, 30 mg.	0.0	0.0
Aluminum, 30 mg.	0.1	0.1
Aluminum, 30 mg.	0.5	0.55
Aluminum, 30 mg.	1.0	1.0
Aluminum, 50 mg.	0.5	0.4
Ferric iron, 10 mg.	1.0	0.9

Determination of titanium. Titanium is precipitated as orange-red $\text{TiO}(\text{C}_6\text{H}_5\text{ON})_2 \cdot 2\text{H}_2\text{O}$ with 8-hydroxyquinoline from solutions containing acetic acid, sodium acetate and tartrate, or from ammoniacal tartrate solutions.

Precipitation is complete over the pH range 4.8-8.6. The precipitate may be weighed as the hydroxyquinolate after drying at 110° C., or as TiO_2 after strong ignition, or it may be titrated bromometrically by the method of Berg.^{98,156,167}

Procedure. To 150 ml. of solution containing 0.1 g. of titanium, add 1 g. of tartaric acid and 0.5 g. of sodium acetate. Add ammonium hydroxide until the solution is neutral to phenolphthalein and then add 1.5 ml. of glacial acetic acid. Heat to 60° C., stir well, and add an excess of 2 per cent alcoholic 8-hydroxyquinoline reagent. Boil the mixture for 10 minutes, filter, wash with hot water, and dry at 110° C. Weigh as $\text{TiO}(\text{C}_9\text{H}_6\text{ON})_2$. The factor for titanium is 0.1361. The precipitate may also be determined by bromate-bromide titration. One ml. of 0.1 N potassium bromate is equivalent to 0.599 mg. of titanium.

This procedure allows for the separation of titanium from alkaline earth and alkali metals. Interference by cadmium, copper, magnesium or zinc can be eliminated by precipitating these metals with 8-hydroxyquinoline from a solution containing sodium hydroxide and sodium tartrate, which prevents the precipitation of titanium. In an acetic acid solution containing malonic acid, titanium is precipitated, but the corresponding complexes of calcium, strontium, barium, magnesium, and the alkali metals are not. If aluminum is present, seventy-five times its weight of malonic acid is added before precipitating with 8-hydroxyquinoline.

According to Claasen,²⁶² Berg's method for precipitating titanium does not always give a quantitative separation. If tartaric acid is present, it is necessary to add a large excess of ammonium sulfate, to heat the solution to boiling, and to keep on a steam bath for 1-2 hours. Not more than 1 gram of tartaric acid must be present, and the pH of the solution should be at least 5.2. Gravimetric results are usually a little high because the precipitate is difficult to wash. Titanium can be separated from aluminum in oxalic acid solutions at pH 5.6-6.5, but Claasen²⁶² states that results are unsatisfactory in solutions of malonic acid.

Titanium can be determined in a mixture containing iron, aluminum, and titanium with the use of 8-hydroxyquinoline.^{105,148} This procedure is described on page 291.

Tzinberg¹⁵⁹ has used 8-hydroxyquinoline to determine titanium in stainless steel, and Arend and Schnellenbach¹⁶⁰ have used a similar method for determining titanium in alloy steels. Wabnitz¹⁵⁸ has described a method for separating titanium from aluminum.

Procedure. To the solution to be analyzed, add 1 g. of tartaric acid and 70-80 times as much malonic acid as is necessary to form a stable complex with aluminum. Neutralize the solution to phenolphthalein with ammonium hydroxide and add a little acetic acid, and precipitate titanium by adding 8-hydroxyquinoline acetate solution mixed with alcohol. Aluminum can be precipitated in the filtrate with the reagent in the presence of ammonium hydroxide.

Determination of zirconium. A voluminous precipitate is formed when a solution of zirconium salt is treated with 8-hydroxyquinoline. Precipitation of

zirconium is complete, but the composition of the precipitate varies from $2 \text{ZrO}_2 \cdot 3 \text{C}_9\text{H}_7\text{ON}$ to $\text{Zr}(\text{C}_9\text{H}_6\text{ON})_4$. According to Balanescu,¹⁶¹ this variability in the composition of the precipitate appears to be due to the degree of dispersion of the aggregates rather than to chemical causes.

For determining 0.3 to 30 mg. of zirconium, the following procedure is recommended:

Procedure. To a solution containing no other metallic ions which are precipitated by the reagent, add 10 ml. of 6 N nitric acid and dilute to 50 ml. Evaporate to a small volume on a water bath. Add an additional 5 ml. of nitric acid and again evaporate. Do not evaporate to dryness. Dilute to 50 ml. with water and add 5-10 ml. of a 3 per cent alcoholic solution of 8-hydroxyquinoline and 50-70 ml. of 2 N sodium or ammonium acetate. Allow to stand for a time and filter. Wash with boiling water containing sodium acetate until the filtrate comes through colorless. Dry at 130-140° C. and weigh as $\text{Zr}(\text{C}_9\text{H}_6\text{ON})_4$ or ignite to ZrO_2 . The factor for zirconium in the hydroxyquinolate is 0.1367.

The final determination may also be made by dissolving the precipitate in 50 per cent sulfuric acid, diluting to 200 ml., adding potassium bromide and a measured excess of standard potassium bromate solution, and then titrating the excess bromine with sodium thiosulfate after adding potassium iodide. One ml. of 0.1 N potassium bromate solution is equivalent to 0.00057 g. of zirconium.

Results obtained with this method show errors ranging from +3.45 to -6.13 per cent.

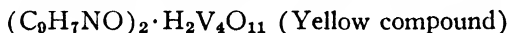
Sue and Wetloff²⁴² recommend the following conditions for precipitating zirconium: Add sufficient tartaric acid to a hydrochloric acid solution of the zirconium salt to form the complex, and add two times the theoretical quantity of 8-hydroxyquinoline in acetic acid. Boil the solution gently and cool before filtration. The slight solubility of the zirconium compound in water causes an error of 1-3 per cent in the gravimetric determination.

Determination of lead. Lead is precipitated quantitatively by 8-hydroxyquinoline from a solution of pH 8.4-12.3. The yellow precipitate of $\text{Pb}(\text{C}_9\text{H}_6\text{ON})_2$ may be weighed after drying at 105° C.^{162,278} Hovorka¹⁶³ has studied the determination of lead by this method, and has found that, for quantities of lead ranging from 0.04 to 0.1 g., results are obtained which are usually about 1 per cent too low. If precipitation takes place in a hot solution, results are somewhat lower than when precipitation takes place in the cold, but in the latter case, filtration is more difficult, and there is a noticeable adsorption of other ions. For the precipitation, 2.5 moles of the reagent are sufficient for 1 atom of lead.

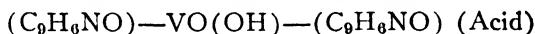
The following procedure may be used:

Procedure. Make the solution to be analyzed acid with acetic acid, and add a saturated solution of 8-hydroxyquinoline. Add ammonium hydroxide until the solution has a slight odor of ammonia. Allow to stand for 2 hours and filter. Wash with a half-saturated solution of the reagent, then with cold water, and weigh after drying at 105° C. The factor for lead is 0.4183. This procedure can be used for the determination of lead in insoluble compounds which dissolve in ammonium acetate.

Determination of vanadium. 8-Hydroxyquinoline reacts with solutions of vanadates in the presence of acetic acid to form a yellow precipitate, which on warming and subsequent cooling changes to a blue-black.^{178,212} The yellow compound is the hydroxyquinolate of tetravanadic acid.



The blue-black compound is the anhydride of the acid



and has the following composition



The precipitation of vanadium by means of 8-hydroxyquinoline is quantitative for the pH range 2.7 to 6.1.¹⁷³ Since precipitation is quantitative, 8-hydroxyquinoline is suitable for the estimation of vanadium.¹⁷⁴

Procedure. To 100 ml. of a solution of sodium vanadate containing 7-124 mg. of V_2O_5 , add a slight excess of 4 per cent 8-hydroxyquinoline in glacial acetic acid. Precipitation is best carried out in a hot solution. The precipitate is ignited to V_2O_5 .

Results obtained with this method agree with those obtained with the more tedious method of Rose. The determination cannot be carried out in the presence of chromate, although this ion can be removed with the aid of quinoline.

Tzinberg¹⁷⁵ has determined vanadium by precipitating as $\text{V}_2\text{O}_3(\text{C}_9\text{H}_6\text{ON})_4$ with 8-hydroxyquinoline, followed by drying at 120°C . and weighing. The results agree with those obtained by ignition to V_2O_5 . The organic complex can also be determined by titration with bromine in alkali or by potassium bromate in an acid solution (page 272).

Vanadium may be determined colorimetrically without first separating from iron by the method of Bach and Trelles.¹⁷⁶

Reagent. Dissolve 2.5 g. of 8-hydroxyquinoline in 100 ml. of a 20 per cent solution of citric acid.

Procedure. Add dilute sulfuric acid to 50 ml. of the solution to be analyzed until just acid to Congo red, and add 5 drops of 8-hydroxyquinoline solution. Shake, add 10 ml. of isoamyl alcohol, and shake again. The alcohol layer is removed and colorimetrically compared with standard solutions of $\text{NaVO}_3 \cdot 4\text{H}_2\text{O}$ similarly prepared.

Copper interferes with this determination but iron does not. The color conforms to Beer's law. In a neutral or slightly acid solution (pH 4-5), pentavalent vanadium salts react with 8-hydroxyquinoline to form a compound $(\text{V}_2\text{O}_3)-(\text{C}_9\text{H}_6\text{ON})_4$, which can be extracted from its aqueous solution with chloroform. Hexavalent chromium compounds do not react and remain in the aqueous layer,¹⁷⁷ and thus may be separated from vanadium.

Results indicate that the separation of vanadium is satisfactory in the presence of 100-200 times as much chromium. Ferric iron and hexavalent molybdenum are also extracted. Aluminum, silicate, phosphate and fluoride do not prevent the extraction of vanadium. Tungsten yields a hydroxyquinolate which is insoluble in chloroform, and unless present in very small quantities should be absent. The vanadium complex may be converted to vanadate by evaporating the chloroform solution to dryness and fusing the residue with sodium carbonate.

Detection of vanadium. Vanadium may be detected by means of the yellow to blue-black precipitate which forms when 8-hydroxyquinoline is added to acetic acid solutions of vanadates.^{177,178}

Procedure. Add a few drops of 2.5 per cent 8-hydroxyquinoline in 6 per cent acetic acid to a neutral or acetic acid solution of a vanadate. Either a yellow or a blue-black precipitate forms. This color is accentuated by extracting with a little chloroform. The extraction is best carried out at a pH corresponding to the intermediate color of methyl orange or bromocresol green.

The sensitivity of this reaction is 1:670,000, which is more delicate than that with hydrogen peroxide.

Alkali salts, silica, aluminum, phosphates, arsenates, fluorides, chlorides, borates, or chromates do not interfere. Ferric iron, small amounts of hexavalent molybdenum, and uranium pass with vanadium into the chloroform layer. Tungsten also yields a precipitate with the reagent in a slightly acid solution.

Interference from molybdenum, tungsten, and titanium can be eliminated by making the vanadium test on the filtrate obtained by treating the solution to be tested as follows: Add sodium carbonate and filter to remove the titanium, and acidify the filtrate with acetic acid and add barium acetate to precipitate the molybdenum and tungsten. In the presence of iron, which gives a brown precipitate with the reagent in an acetic acid solution, precipitation with sodium carbonate is not satisfactory, since the iron precipitate retains an appreciable amount of vanadium. To remove iron, treat 2 ml. of the solution to be tested with 0.5 ml. of 33 per cent sodium hydroxide solution and filter. Apply the vanadium test to the filtrate.

Very small quantities of vanadium can be detected by the method of Bach.¹⁷⁹

Procedure. Place 100 ml. of the solution to be tested in a 100-ml. Nessler tube fitted with a ground glass stopper and having an internal diameter of 3 cm. Make this solution alkaline to litmus with ammonium hydroxide and add 5 drops of 2.5 per cent 8-hydroxyquinoline in 10 per cent acetic acid. Stir and extract the color with 10 ml. of isoamyl alcohol. Vanadium is indicated by a red color in the alcohol layer. The sensitiveness of this reaction is 1:17 million.

Vanadium in chloroform solution yields a reddish color when treated with 8-hydroxyquinoline, and the subsequent addition of sodium azide causes the color to change to green.³⁰¹ The latter reaction is more selective than the former, and in pure solutions is sensitive to 0.05 γ vanadium in 0.15 ml. of chloroform.

Vanadium can be detected by its catalytic effect on the reaction between aniline and potassium chlorate.¹⁸⁰ As little as 0.001g of vanadium produces a noticeable effect, although in the presence of 8-hydroxyquinoline the test is ten times as sensitive. Ferric iron interferes, but this can be prevented by adding 0.05 g. of sodium hydrogen fluoride. Bismuth and copper interfere.

Similar reactions between potassium chlorate and p-aminophenol, potassium periodate and di-o-anisidine, potassium chlorate and p-phenetidine, potassium bromate and p-phenetidine, and potassium periodate and p-phenetidine have been used successfully for the detection of vanadium. In all cases, 8-hydroxyquinoline enhances the catalytic action of vanadium.¹⁸⁰

Thanheiser and Waterkamp¹⁸¹ have used 8-hydroxyquinoline to detect vanadium in steel by means of a spot method. The surface of the steel is well cleaned, then treated with a drop of mineral acid, and the drop of solution which is obtained is tested for vanadium on a spot plate.

Detection and determination of tungsten. Tungstates react with 8-hydroxyquinoline in much the same manner as vanadates. Precipitation is complete at pH 4.95-6.56. In cold solutions a precipitate of 8-hydroxyquinoline tungstate is formed in which the tungsten content varies with the acidity of the solution. From hot solutions, however, the precipitate corresponds to the formula $(C_9H_6ON)_2WO_2$.¹⁶⁴ Precipitation is quantitative when the method of Halberstadt is used.¹⁶⁵

Procedure. Make the dilute solution of the tungstate neutral or slightly alkaline, and add an excess of a 4 per cent solution of 8-hydroxyquinoline in ethyl alcohol. Heat to boiling and add acetic acid until the mixture is acid. Boil, filter, and wash the precipitate with hot water, and then dry at 120° C. and weigh. The precipitate contains 36.5 per cent tungsten.

When solutions containing tungstates are acidified with acetic acid, polytungstates are formed, and this explains the impossibility of obtaining accurate results when the tungstate sample is acidified with acetic acid as a preliminary treatment. Low results obtained by titrating ammonium tungstate are due to the same effect.¹⁶⁴ According to Halberstadt¹⁶⁶ the WO_3 in a solution of sodium tungstate is accurately precipitated from a solution buffered with a phosphate, borate, or acetate at a pH of 3.3-3.5, but not if the pH is higher or lower than this range. Results are similar if WO_3 is in the form of a phosphotungstate, and for this reason the 8-hydroxyquinoline method is useful in biological determinations.

Jilek and Rysanek¹⁶⁷ precipitate tungsten from an oxalate-ammonium acetate solution, and ignite the residue to WO_3 .

Procedure. To a tungstate solution containing not more than 0.1 g. of tungsten, add 5 g. of oxalic acid and 5 g. of ammonium acetate. Dilute to 150-200 ml. and neutralize with ammonium hydroxide to methyl red. Heat to 60-80° C. and add 2 ml. of a solution prepared by dissolving 20 g. of 8-hydroxyquinoline in 50 ml. of glacial acetic acid. Let stand for 1-2 hours and filter. Wash the precipitate with hot oxalic acid-ammonium acetate buffer solution to

which 1 ml. of reagent has been added. Ignite to constant weight at 800°C . and weigh as WO_3 .

A titrimetric method based on bromination with a potassium bromate-potassium bromide mixture has been used with good results by Merz¹⁶⁸ (page 272).

An attempt to determine tungsten by the centrifugal determination of the volume of the 8-hydroxyquinoline precipitate did not yield satisfactory results.⁸⁰

Canticao¹⁶⁹ has used 8-hydroxyquinoline to determine tungsten in minerals, and Mukhina¹⁷⁰ has reviewed the use of this reagent for the determination of tungsten in steels and alloys.

Since the precipitation of tungsten with 8-hydroxyquinoline as $\text{WO}_2\cdot(\text{C}_9\text{H}_6\text{ON})_2$ is complete at pH 4.95-5.65, and cadmium precipitation with the same reagent is complete at pH 5.66-14.58, it is possible to separate these metals by a proper control of acidity before adding the precipitant.¹⁷¹

Jilek and Rysanek¹⁷² have described a method for determining tungsten in the presence of tin.

Determination of molybdenum. Molybdenum is precipitated from solutions of alkali molybdates by the addition of 8-hydroxyquinoline. Precipitation is quantitative from solutions of pH ranging from 3.3 to 7.6.¹⁷⁸ When the precipitate is dried at $130\text{--}140^{\circ}\text{C}$. it corresponds in composition to the formula $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$. The usual titrimetric procedure cannot be used, for it is a singular fact that the molybdenum complex, after drying, is insoluble in both alkalies and acids, and is not soluble even in aqua regia.⁶⁰

Geilmann and Weibke¹⁸² determine molybdenum by adding a 5 per cent solution of 8-hydroxyquinoline to a solution of an alkali molybdate which has been neutralized to methyl red, treated with a few drops of dilute sulfuric acid, and then buffered with 5 ml. of 2 N ammonium acetate. Under these conditions molybdenum is precipitated quantitatively in a weighable form.

Ishimaru¹⁸³ has studied the proper drying temperatures for the hydroxyquinolates of tungsten, vanadium, and molybdenum and recommends the following:

TABLE 45.

Metal	Formula of Salt	Drying Temperature
Tungsten	$\text{WO}_2(\text{C}_9\text{H}_6\text{ON})_2$	$95\text{--}128^{\circ}\text{C}$.
Vanadium	$\text{V}_2\text{O}_5(\text{C}_9\text{H}_6\text{ON})_4$	$120\text{--}154^{\circ}\text{C}$.
Molybdenum	$\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$	$135\text{--}159^{\circ}\text{C}$.

TABLE 46.

Metal	Ignited to	Ignition Temperature
Tungsten	WO_3	$>420^{\circ}\text{C}$.
Vanadium	V_2O_5	$>468^{\circ}\text{C}$.
Molybdenum	MoO_3	$505\text{--}548^{\circ}\text{C}$.

The metals in Table 45 are frequently determined after precipitation with 8-hydroxyquinoline by igniting the hydroxyquinolates with oxalic acid to form the oxides. Ishimaru¹⁸⁸ recommends the following ignition temperatures in Table 46.

Molybdenum may be separated from plant materials as a preliminary concentration for spectrographic analysis.²⁷²

Lelubre²⁸² claims that use of 8-hydroxyquinoline as a molybdenum reagent involves an unnecessary expense, since precipitation as lead molybdate or molybdenum sulfide is satisfactory.

Separation of molybdenum. Molybdenum may be separated from magnesium, copper, cobalt, zinc, rhenium, and phosphate by means of 8-hydroxyquinoline.

Separation of molybdenum and cobalt. Molybdenum and cobalt may be separated by the following procedure:⁶⁰

Procedure. Add 5 g. of ammonium acetate to 80 ml. of the solution to be analyzed and heat to boiling. Add 60 ml. of N sodium hydroxide and 10 ml. of 5 per cent 8-hydroxyquinoline in 2 N acetic acid. Boil for 5 minutes, filter off the complex cobalt compound, and precipitate molybdenum by adding 7.55 ml. of glacial acetic acid to the filtrate.

Separation of molybdenum and zinc. Molybdenum and zinc are separated as follows:⁶⁰

Procedure. Add 5 g. of ammonium acetate and 40 ml. of 2 N sodium hydroxide to 80 ml. of the solution to be analyzed. Heat to boiling and precipitate zinc hydroxyquinolate by adding 10 ml. of a 5 per cent solution of 8-hydroxyquinoline in 2 N acetic acid. Filter, and precipitate molybdenum by adding 8.5 ml. of glacial acetic acid to the filtrate.

Separation of molybdenum and rhenium. Molybdenum is precipitated with 8-hydroxyquinoline from solutions of rhenium by the following method:^{182,184}

Procedure. Make the solution containing an alkali molybdate and perrhenate neutral to methyl red, add a few drops of dilute sulfuric acid, and 5 ml. of 2 N ammonium acetate. Precipitate molybdenum with a 5 per cent solution 8-hydroxyquinoline. Precipitation is quantitative. Rhenium can be precipitated with nitron from the filtrate obtained after removing the molybdenum complex by filtration.

Separation of molybdenum and phosphate. Molybdenum can be precipitated in the presence of an acetate buffer with 8-hydroxyquinoline without interference from phosphate.¹⁸⁵ Phosphate may be determined in the filtrate, after filtering off the molybdenum, by means of ammonium molybdate in the usual manner.

Detection of molybdate, tungstate, and vanadate. Montequi^{186,187} has used 8-hydroxyquinoline as a precipitant for a group of anions consisting of molybdate, tungstate and vanadate in a systematic scheme of analysis. The precipitating reagent is an acetic acid solution of 8-hydroxyquinoline.

Detection and determination of uranium. Soluble uranyl salts give a deep red precipitate of $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot \text{C}_9\text{H}_7\text{ON}$, which is stable up to 200°C . The precipitate can be weighed after drying at 105°C .; it may be titrated with bromine in the usual manner; or it may be weighed as U_3O_8 after strong ignition.¹⁸⁸ Precipitation is best carried out in a hot, dilute acetic acid solution by adding 8-hydroxyquinoline acetate solution. The reagent is added until red crystals appear, and is then added dropwise until precipitation is complete. If mineral acids are present, add ammonium acetate. Cool, filter, and wash the precipitate with water. Finally weigh after drying at 105°C . The factor for uranium is 0.3385.

Hecht and Krafft-Ebing¹⁸⁹ have proposed a scheme for the separation and determination of tetravalent uranium. Kroupa^{190,191} has used 8-hydroxyquinoline for determining uranium in radioactive minerals, and Hecht and Korisch¹⁹² have used the same reagent for determining uranium in zircon.

Determination of columbium. Columbium may be determined with 8-hydroxyquinoline by the method of Sue.¹⁹³

Procedure. To a solution containing about 40 mg. of Cb_2O_5 in 120-150 ml., add 0.2-0.5 g. of oxalic acid and 5 ml. of 10 per cent ammonium acetate solution. Add ammonium hydroxide dropwise until the solution is neutral to phenolphthalein. Heat to 70°C . and add a slight excess of a solution prepared by dissolving 3 g. of 8-hydroxyquinoline in 100 ml. of 70 per cent alcohol. Boil for 30 minutes, allow to stand 15 minutes and filter. Wash with 125 ml. of warm water, and dry at 105°C . and weigh or titrate bromimetrically as recommended by Berg²⁹⁸ (page 272). The factor for columbium pentachloride is 0.2678.

The probable composition of the precipitate is $\text{Cb}_2\text{O}_5 \cdot 5.5\text{C}_9\text{H}_7\text{ON} \cdot 4\text{H}_2\text{O}$.

Schwarz¹⁹⁴ has investigated the possibility of using 8-hydroxyquinoline for the separation and determination of tantalum and columbium but without important results.

Determination of chromium. Chromium forms the compound $\text{Cr}(\text{C}_9\text{H}_6\text{ON})_3$ with 8-hydroxyquinoline, and precipitation is nearly quantitative when carried out as follows:¹⁹⁵

Procedure. Add ammonium hydroxide to 10 ml. of a solution containing chromium until a faint permanent precipitate of chromic hydroxide appears. Add just enough sulfuric acid to dissolve the precipitate and heat to 70°C . To the hot solution add 20 ml. of 2 per cent 8-hydroxyquinoline in 2 N acetic acid and then 20 ml. of N sodium hydroxide and 20 ml. of 4 N ammonium acetate. Boil for 1 minute, filter through sintered glass, wash with hot water, dry at $105\text{-}110^\circ \text{C}$. and weigh. The factor for chromium is 0.1074.

Determination of bismuth. In an acetic acid or ammoniacal tartrate solution, bismuth reacts with 8-hydroxyquinoline to form an orange-yellow, crystalline precipitate of $\text{Bi}(\text{C}_9\text{H}_6\text{ON})_3 \cdot \text{H}_2\text{O}$. The precipitate may be weighed in this form after drying at 105°C . After long heating at $130\text{--}140^\circ \text{C}$. the precipitate becomes anhydrous.

The following gravimetric method may be used.^{196,197,279}

Reagent. A 4 per cent solution of 8-hydroxyquinoline in 8 per cent acetic acid.

Procedure. To a solution of bismuth sulfate or nitrate, add 30 ml. of 50 per cent tartaric acid for each 0.1 g. of bismuth. Add 4 drops of phenolphthalein indicator and 4 drops of methyl red indicator and add ammonium hydroxide until a faint red color appears, and then add 10 per cent acetic acid until the color changes first to yellow and then to pink. Add sufficient acetic acid to make the acid concentration 1 per cent, and enough ammonium acetate to make the concentration 3 per cent. Heat the mixture to $60\text{--}70^\circ \text{C}$. and add dropwise a quantity of 8-hydroxyquinoline that is four times that required to precipitate all the bismuth. Heat to boiling and allow to cool. Collect the precipitate in a tarred porcelain crucible and wash with hot water. Dry at $100\text{--}105^\circ \text{C}$. and weigh as $\text{Bi}(\text{C}_9\text{H}_6\text{ON})_3 \cdot \text{H}_2\text{O}$. The factor for bismuth is 0.3171.

Attempts to determine bismuth as $(\text{C}_9\text{H}_7\text{ON}) \cdot \text{HBiI}_4$ gravimetrically have not been entirely satisfactory, although Berg and Wurm¹⁹⁸ have based a titrimetric method upon the formation of this precipitate.

Reagents. *8-hydroxyquinoline reagent:* Dissolve 5 g. of 8-hydroxyquinoline in 100 ml. of 0.2 N sulfuric acid.

Wash solution: Mix 50 ml. of 2 N sulfuric acid, 25 ml. of 0.1 N potassium iodide, 18 g. 8-hydroxyquinoline and a few crystals of hydrazine sulfate and dilute with water to 1 liter.

Procedure. To the cold bismuth solution containing sulfuric or nitric acid, add an excess of 8-hydroxyquinoline and 0.1 N potassium iodide. Filter immediately and wash the precipitate thoroughly with the wash solution. Dissolve in 10 per cent hydrochloric acid and titrate by the potassium-iodate-acetone method of Berg³¹³ (page 396). One ml. 0.1 N potassium iodate solution corresponds to 0.0017417 g. bismuth.

Kolthoff and Griffith¹⁹⁹ have studied the method of Berg and Wurm and have found that generally it gives values which are about 1 per cent too low. Experiments also reveal that in carrying out this procedure the final concentrations of sulfuric acid, nitric acid, or perchloric acid may be as high as 1 N, but low results are obtained if the chloride concentration is above 0.08 N. With 0.3 N chloride concentration results may be 7.5 per cent too low, and the filtrate contains considerable bismuth. An excess of 0.001 mole of potassium iodide appears to be sufficient. The precipitate is appreciably soluble, and results are usually within 0.3 per cent of the correct value unless the quantity of bismuth is small. With small quantities of bismuth, results vary according to the method of washing the precipitate. Better results are obtained by titrat-

ing the excess of iodide than by the direct titration of the hydrochloric acid solution of the precipitate. The L. W. Andrews method of titrating with potassium iodate to iodine chloride²⁰⁰ has been found preferable to the method of Lang.

Bismuth may also be determined by a polarimetric titration: ²⁸⁰

Procedure. To 10 ml. of bismuth solution in 20 per cent nitric acid, add 2 g. of sodium tartrate, and add 1.0 N sodium hydroxide until the mixture is neutral to methyl red. Add 7.33 g. of sodium acetate trihydrate (pH = about 9) and 0.16 ml. of 6 N acetic acid. Adjust the potential to 850 mv. and suppress the maximum with 50 drops of 0.1 per cent phenolphthalein in ethyl alcohol. Titrate with a 2 per cent solution of 8-hydroxyquinoline in 1.0 N acetic acid.

Bismuth may be determined colorimetrically by dissolving the hydroxyquinolate in hydrochloric acid and treating the resulting solution with Folin's reagent. The color is compared with that produced by standard solutions containing known quantities of bismuth.⁷⁸ With this method 0.005-0.05 mg. of bismuth can be determined.

Sazerac and Pouzergues²⁰¹ have determined bismuth colorimetrically as follows:

Reagent. Dissolve 2 g. of 8-hydroxyquinoline in 100 ml. of water, containing 0.3 ml. of nitric acid. Just before use, mix with an equal volume of 4 per cent potassium iodide solution.

Procedure. Shake 2 ml. of the solution to be analyzed with 0.2 ml. of the reagent and 1.5 ml. of a mixture composed of 1 volume of amyl acetate and 2 volumes of acetone. The dissolved complex is red-orange or red-violet in color, and can be determined colorimetrically at bismuth concentrations ranging from 2 to 100 mg. The reaction will detect 0.000005 mg. of bismuth. Cyclohexanol may also be used for the extraction of the colored compound.

Farini²⁰² has studied various methods for determining bismuth and recommends the gravimetric precipitation as the phosphate, and the titrimetric determination as the hydroxyquinolate.

Detection of bismuth. Bismuth can be detected by the orange colored precipitate which is formed when solutions of bismuth salts are treated with potassium iodide and 8-hydroxyquinoline.^{203,205}

Reagent. Add 2 g. of 8-hydroxyquinoline to 100 ml. of water and add a few drops of nitric or sulfuric acid to effect solution.

Procedure. Mix a few ml. of the above reagent with an equal volume of 4 per cent potassium iodide solution, and pour the resulting mixture into the solution to be tested. Solutions containing bismuth at a concentration of 1:100,000 immediately give a flocculent orange precipitate. The test is made more sensitive by extracting the color with cyclohexanol or with acetone and amyl acetate.

Ferric salts give a green coloration with the same reagent.

Bismuth can be identified in cells and animal tissues by the formation of orange-red crystals of the double iodide of bismuth and 8-hydroxyquinoline.²⁰⁴

Determination of antimony. Antimony is quantitatively precipitated with 8-hydroxyquinoline from a solution of pH 6.0-7.5. The following procedure has been proposed by Pirtea:²⁰⁶

Reagent. Dissolve 7-8 g. of 8-hydroxyquinoline in as little glacial acetic acid as possible and dilute with 200 ml. of water. Add 6 N ammonium hydroxide until a slight turbidity remains, and dissolve this precipitate with a drop of acetic acid.

Procedure. To the sample solution containing 0.5-1.5 g. of antimony and an excess of hydrochloric acid, add 30 ml. of the reagent. Heat to 60-70° C. and neutralize carefully with 10 per cent ammonia solution. A yellow precipitate begins to form at pH 1.5, and precipitation is complete at about pH 6.0-7.5. At this point the color of the solution is yellow. Continue to heat for a short time, and rotate the beaker so as to cause the precipitate to collect on the bottom. If the odor of acetic acid is still perceptible, add sufficient ammonium hydroxide to leave a faint odor of ammonia. Allow the mixture to stand 2 hours and filter through a filter crucible. Wash the precipitate with a cold solution containing 0.2-0.4 g. of 8-hydroxyquinoline and a few drops of acetic acid per liter until the filtrate gives no test for halogen with silver nitrate and nitric acid. Dry to constant weight at 105-110° C. The precipitate is yellow and contains 21.97 per cent antimony.

The results reported with this method agree within 1 mg. of the true value.

Detection of antimony. Antimony can be detected by means of the yellow precipitate which forms when 8-hydroxyquinoline is added to solutions of antimony trichloride or tarter emetic. Precipitation is quantitative at pH 6.0-7.5. As little as 12γ of antimony can be detected in 5 ml. of a solution of antimony trichloride.²⁰⁶

Determination of copper. Copper is precipitated by 8-hydroxyquinoline in acetic, ammoniacal and sodium hydroxide solutions of pH 5.33-14.55 to form a green complex corresponding to the formula $\text{Cu}(\text{C}_9\text{H}_6\text{ON})_2$. In the presence of sodium tartrate, either in acetic acid or ammoniacal solution, copper can be precipitated with 8-hydroxyquinoline without interference from aluminum, magnesium, beryllium, manganese, zinc, cadmium, or moderate amounts of iron.²⁰⁷

Berg²⁰⁸ describes a method for precipitating copper with 8-hydroxyquinoline, either in acetic acid solution or in a sodium hydroxide solution containing a tartrate.

Precipitation in acetic acid. To a solution containing 0.12 g. of copper, or less, in 100 ml. of solution, add 5 g. of sodium acetate and sufficient acetic acid to make the acid concentration 10 per cent. Heat to 60° C. and add dropwise a slight excess of a 2 per cent solution of the reagent in alcohol. Slowly raise the temperature to 90° C. and filter. Wash with hot water, and dry at

110° C. and weigh, or dissolve the precipitate in acid and determine iodometrically (page 272).

Precipitation in sodium hydroxide. Add 3-5 g. of tartaric acid to the copper solution and neutralize with 20 per cent sodium hydroxide. Add 15 ml. of 2 N sodium hydroxide in excess, and proceed as in the presence of acetic acid. The copper precipitate contains 18.08 per cent copper.

Shik²⁰⁹ claims that the determination of copper with 8-hydroxyquinoline in a pure salt solution and in the presence of acetic acid gives an error of 0.4-0.6 per cent. An error of 1 per cent or more is obtained in the determination of copper in the presence of magnesium, calcium, and manganese, although according to Shik, accurate results are obtained in the presence of sodium hydroxide and sodium tartrate.

The following method is due to Calvet:²⁰⁷

Procedure. Heat 200 ml. of a neutral solution containing 0.1 g. of copper to 70-80° C. and add 3 g. of sodium tartrate. Add a slight excess of 3 per cent 8-hydroxyquinoline in 2 N acetic acid. Cool, filter, wash, dry at 108-110° C., and weigh.

The compound contains 18.08 per cent copper. The author claims for this method an accuracy equal to that of the electrolytic method.

Tzinberg²¹⁰ has proposed a method for the rapid determination of copper in the presence of other metals. This method is based on the insolubility of the copper hydroxyquinolate and the solubility of other metal hydroxyquinolates in nitric acid of definite concentration.

Copper can be determined by titrating the acid liberated when copper is precipitated with 8-hydroxyquinoline.¹⁷ The procedure is the same as that described for magnesium (page 273).

Copper may be determined polarographically after precipitating as the hydroxyquinolate.²⁶¹ Copper may also be recovered from plant materials with the aid of 8-hydroxyquinoline as a concentration method for spectrographic analysis.²⁷²

Fleck and Ward⁶⁰ have also studied the precipitation of copper with 8-hydroxyquinoline. Frommes²⁷⁷ has reviewed the use of 8-hydroxyquinoline in the determination of copper.

Separation of copper. A number of important separations involving copper can be accomplished with the aid of 8-hydroxyquinoline.

Separation of copper from iron, bismuth, stannic tin, pentavalent arsenic and antimony. Trivalent iron and bismuth, stannic tin, and pentavalent arsenic and antimony interfere with the iodometric determination of copper. Pure precipitates of copper can be obtained from alkaline solutions containing the above ions with 8-hydroxyquinoline. These precipitates give good results by iodometric titration.²¹¹

Separation of copper and cadmium. Copper and cadmium can be separated with the aid of 8-hydroxyquinoline. The copper complex is insoluble in

10 per cent acetic acid, while the corresponding cadmium compound is readily soluble.¹⁰⁴ According to Tzinberg²¹⁰ these two metals are separated as follows:

Procedure. To a solution containing about 0.05 g. of copper and the same quantity of cadmium, add 3 g. of tartaric acid and dilute to 125 ml. Neutralize with ammonium hydroxide to methyl red and add 15 ml. of 10 per cent nitric acid. Precipitate copper with a slight excess of 2 per cent alcoholic 8-hydroxyquinoline. Heat the solution to 70° C., cool, and filter. Determine copper in the usual manner.

Separation of copper and zinc. Zinc and copper in brass can be determined by using the above procedure (copper and cadmium).²¹⁰

Detection of copper. Copper may be detected with 8-hydroxyquinoline using a spot technique.²¹²

Procedure. Place a drop of a saturated solution of 8-hydroxyquinoline in 80 per cent acetic acid on a strip of filter paper, and in the middle of the resulting spot place a drop of the solution to be tested. After a moment add another drop of reagent to the middle of the spot, and then add a drop of a 25 per cent solution of potassium cyanide. If copper is present, a raspberry-red color is formed.

This test is due to the solution of the copper precipitate with the formation of $[\text{Cu}_2(\text{CN})_6]^{-4}$ and $(\text{CN})_2$. The latter reacts with the reagent to form a red compound. This reaction is very sensitive and will detect as little as 0.0004 mg. of copper. If uranyl or ferric ions are present an excess of ammonia is added to the original solution and the resulting precipitate removed by filtration. Uranyl ions cause a brown spot in the above test and ferric ions a black spot. As little as 0.002 mg. of copper can be detected in the presence of 400 times as much iron.

Determination of nickel. Nickel forms a greenish precipitate of $\text{Ni}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$ with 8-hydroxyquinoline. Precipitation is complete over the pH range 4.3-14.6. The precipitate may be dried and weighed (precipitate becomes anhydrous when dried at 130° C.) or titrated in the usual manner using potassium bromate-potassium bromide²¹³ (page 272). The gravimetric method is not very satisfactory, since the composition of the precipitate obtained after drying at 120° C. is indefinite. The titrimetric method gives excellent results.

Nickel can also be titrated with 8-hydroxyquinoline by a filtration method.²¹⁴ By this procedure, the end point is determined by adding the reagent from a buret to the nickel solution, filtering and adding more reagent to the filtrate until no more precipitate forms. The titration is carried out in the presence of sodium acetate and acetic acid.

The centrifugal-volumetric method of Uzumasa and Kayama⁸⁰ for determining the volume of the nickel hydroxyquinolate precipitate is not very accurate. 8-Hydroxyquinoline may be used to recover nickel from plant materials as a preliminary to spectrographic analysis.²⁷²

The precipitation of nickel with 8-hydroxyquinoline has been studied by Fleck and Ward.⁸⁰

Determination of cobalt. A flesh colored precipitate of cobalt hydroxyquinolate is formed when 8-hydroxyquinoline is added to a solution of a cobalt salt.²¹³ Precipitation is complete over the pH range 4.3-14.5. This reaction has been used by Tzinberg²¹⁵ in a titrimetric method for the determination of cobalt in alloys:

Procedure. Ignite a sample of the alloy in a platinum crucible and fuse the residue with a mixture of sodium carbonate and potassium carbonate for 2 hours. Leach the melt with hot water and filter. Dissolve the residue in hydrochloric acid and add 2 g. of ammonium chloride, and precipitate iron with ammonium hydroxide. Filter, add 3 g. of sodium acetate to the filtrate, and make slightly acid with acetic acid. Heat to 70° C. and add a slight excess of a 2 per cent alcoholic solution of 8-hydroxyquinoline. Boil, let stand for 5-10 minutes, and filter off the precipitate of cobalt hydroxyquinolate. Titrate the precipitate bromimetrically according to the method of Berg (page 272).

A titration method similar to that for nickel²¹⁴ can also be used for cobalt. This gives excellent results. Results reported for gravimetric determinations are often unsatisfactory, since the composition of the precipitate which has been dried at 120° C. is indefinite.

8-Hydroxyquinoline may be used for the recovery of cobalt from plant materials as a preliminary to a spectrographic analysis.²⁷² Cobalt is precipitated at pH 5.1-5.2. Ferric or aluminum hydroxyquinolate serves as a collector.

The precipitation of cobalt with 8-hydroxyquinoline has been studied by Fleck and Ward.⁶⁰

Determination of iron. Ferric salts in the presence of as much as 25 per cent acetic acid and sodium acetate yield greenish-black $\text{Fe}(\text{C}_9\text{H}_6\text{ON})_3$. Precipitation is quantitative. The factor for iron is 0.1144. Iron may be estimated by weighing the hydroxyquinolate after drying at 120° C., or after igniting to Fe_2O_3 . The precipitate may also be titrated according to the method of Berg^{98,213,216} (page 272).

Iron may be determined colorimetrically in organic matter as follows:²¹⁶

Procedure. Ash a quantity of the material to be analyzed containing 0.05-0.5 mg. of iron and dissolve in 5 ml. of 18 per cent hydrochloric acid and 35 ml. of water. Ash in a porcelain dish. Do not use platinum. Transfer to a centrifuge tube and add 3 drops of glacial acetic acid, 3 drops of methyl red indicator and 1 ml. of 2 per cent sodium oxalate solution. Add a 5 per cent sodium hydroxide solution until the color of the solution is yellow. Then add 2 ml. of 2.5 per cent solution of 8-hydroxyquinoline in glacial acetic acid, and 0.25 N sodium hydroxide dropwise until the solution turns yellow. Heat in a boiling water bath, and centrifuge while warm. Decant the supernatant liquid, wash with water, and again centrifuge and decant. Dissolve the precipitate in 95 per cent alcohol, add 2 drops of 0.25 N sodium hydroxide, and dilute to 50 ml. Compare the resulting green color with the color of standard solutions similarly prepared.

Iron may be determined in aluminum by the method of Strauss.²¹⁷

Procedure. Precipitate the hydroxides of iron and aluminum in the usual manner and dissolve in hydrochloric acid. Add 3 g. of sodium tartrate, 3 g. of sodium acetate, and 6 ml. of acetic acid. Precipitate iron with a 4 per cent solution of 8-hydroxyquinoline. The precipitate is titrated with potassium bromate-potassium bromide according to the method of Berg (page 272).

The precipitation of iron with 8-hydroxyquinoline has also been studied by Chirnside and co-workers.⁶¹

According to Navez²⁴ the determination of iron can be made more accurately by a modified Berg method. Titration is preferred, for, although less accurate, it is much more rapid than the gravimetric method.

Iron can be separated from the alkaline earths, beryllium, and manganese and aluminum by means of 8-hydroxyquinoline. For the separation of iron from the alkaline earths, precipitate iron in the presence of acetic acid and filter.²¹³ Iron is separated from beryllium similarly.

For the separation of iron from manganese, it is best to precipitate manganese with 8-hydroxyquinoline in an ammoniacal solution. Manganese hydroxyquinolate is very sensitive to acids, and in this respect resembles that of magnesium.²¹³ Iron can be determined in the presence of aluminum by masking aluminum with malonic acid and precipitating iron in an acetic acid solution.²¹³

Determination of manganese. Manganese can be precipitated quantitatively with 8-hydroxyquinoline as a dull-yellow, crystalline compound having the formula $\text{Mn}(\text{C}_6\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$. Precipitation may be made from neutral or weakly acid solutions containing sodium acetate and a small amount of sulfite or hydroxylamine. An alcoholic solution of the reagent is used. Precipitation may also be made from a mineral acid solution containing an excess of an acetic acid solution of the reagent by adding ammonium hydroxide until the solution is weakly alkaline.²¹⁸ Precipitation is complete over the pH range 5.9-10.0

Van der Marel⁸¹ uses a modified Berg method for the gravimetric determination of manganese.

Procedure. To 500 ml. of a neutral solution, containing not more than 0.1 g. of manganous oxide, add 15 g. of ammonium chloride, and make alkaline with ammonium hydroxide. Add sufficient 5 per cent 8-hydroxyquinoline to impart a brownish-yellow color to the solution. Allow the mixture to stand 2 hours on a water bath at 80° C., and filter through a 1G4 Jena crucible. Wash 3 times with 1 per cent ammonium hydroxide and dry 2 hours at 155° C. and weigh. The precipitate contains 16.03 per cent manganese. Results are accurate down to 7 mg. of manganous oxide.

According to Neelakantam,²¹⁸ the manganese precipitate cannot be dried to constant weight at 110° C., and above this temperature there is decomposition. Berg²¹⁸ ignited the precipitate to mangano-manganic oxide with oxalic acid, but the composition of the oxide depends on the temperature and the surrounding atmosphere.²¹⁹

Uzamasa and Kayama⁸⁰ have attempted to determine manganese by the centrifugal volumetric determination of the volume of the manganese hydroxyquinolate precipitate, but the results were not very accurate.

8-Hydroxyquinoline may be used to separate manganese from calcium and zinc. Zinc forms a precipitate of the hydroxyquinolate at acid concentrations in which the $\text{pH} < 5$, while manganese requires a higher pH value.²¹³

Determination of cerium. Solutions of cerous salts containing ammonia and sodium tartrate give a greenish-gray precipitate of $\text{Ce}(\text{C}_9\text{H}_6\text{ON})_3$ when treated with 8-hydroxyquinoline. This reaction is satisfactory for determining 10-50 mg. of cerium. The procedure of Pirtea²²⁰ gives good results.

Procedure. To 20-40 ml. of a neutral solution containing up to 0.1 g. of cerous ion, add 5 ml. of 2 N acetic acid and a slight excess of a 3 per cent solution of 8-hydroxyquinoline in ethyl alcohol. Add from a pipet a 10 per cent solution of ammonia until cerium is precipitated. At first this precipitate is yellow-orange in color, but this slowly turns to a brownish-purple color. The latter compound has the more definite composition. Allow to stand until the change in color is complete, and heat to boiling. Filter through a glass filter crucible. Wash with hot water, dry and weigh. The precipitate has the formula $\text{Ce}(\text{C}_9\text{H}_6\text{ON})_4 \cdot 2\text{H}_2\text{O}$, and contains 18.73 per cent cerium.

It will be observed from the formula of the precipitate that during the reaction with 8-hydroxyquinoline trivalent cerium is oxidized to the tetravalent state. Any ceric ions are first reduced to the cerous state with hydroxylamine hydrochloride until the solution is colorless.²²¹ Results obtained by this method are excellent, but the time required for the transformation to the ceric salt is so great that it is more practicable to ignite the precipitate and weigh as CeO_2 . This procedure also gives good results.

When both thorium and cerous salts are present in the same solution, thorium may be precipitated with 8-hydroxyquinoline in the presence of acetic acid as $\text{Th}(\text{C}_9\text{H}_6\text{ON})_4 \cdot \text{C}_9\text{H}_7\text{ON}$. After the precipitate is filtered and washed, cerium can be precipitated from the filtrate by adding 10 ml. of concentrated sodium tartrate solution, heating to 60° C., making distinctly ammoniacal, and then adding more 8-hydroxyquinoline solution.²²¹

The separation of cerium and thorium has also been studied by Mannelli.²²²

Determination of thorium. A precipitate of $\text{Th}(\text{C}_9\text{H}_6\text{ON})_4 \cdot \text{C}_9\text{H}_7\text{ON}$ is obtained by adding 8-hydroxyquinoline to an acetic acid solution of thorium buffered with ammonium acetate. Precipitation is complete over the pH range 4.4-8.8. The precipitate is suitable both for the macro- and microdetermination of thorium. The procedure is simpler and more rapid than the picrolonate method of Hecht.^{223,270} According to Hecht and Reich-Rohrwig¹⁸⁸ thorium may best be determined as follows:

Procedure. Add 5 g. of sodium acetate to the solution to be analyzed and make neutral to phenol red. Heat to 50° C. and precipitate by adding a solution of 8-hydroxyquinoline in 2-4 per cent acetic acid. Heat at 70° C. until the original yellow precipitate becomes light red in color. Cool and add a little

sodium hydroxide to decrease the acetic acid concentration to 0.3 per cent. Filter and wash with hot water and finally with 25 per cent alcohol. Dry at 170° C. and weigh.

This method is recommended by Wenger and Duckert²⁷¹ for the detection of thorium. As little as 3γ of thorium may be detected by a drop reaction.

Determination of lanthanum. $\text{La}(\text{C}_9\text{H}_6\text{ON})_3$ is precipitated by adding 8-hydroxyquinoline to a dilute acetic acid solution of lanthanum nitrate, and then adding ammonium hydroxide until the solution is strongly ammoniacal. The precipitate may be dried at 130° C. and weighed, or it may be dissolved in 2 N hydrochloric acid and titrated bromimetrically (page 272). The lanthanum precipitate contains 24.33 per cent lanthanum. One ml. of 0.1 N potassium bromate is equivalent to 0.001167 g. lanthanum. Excellent results are claimed with this method.²²⁴

Determination of the rare earths. Metals of the rare earth group are precipitated quantitatively with 8-hydroxyquinoline. They form hydroxyquinolates of definite composition which can be weighed or titrated with potassium bromate and potassium bromide in the usual manner^{222,288} (page 272).

Determination of phosphorus. Phosphoric acid or acid solutions of metallic phosphates react with ammonium molybdate and 8-hydroxyquinoline to form an insoluble orange-colored addition compound which may be used for the determination of phosphorus. This precipitate may be dried and weighed or determined titrimetrically by the method of Berg²²⁵ (page 272).

A method for the determination of phosphorus in biological materials is described by Scharrer.²²⁶

Reagent. Mix 42 ml. of concentrated hydrochloric acid, 42 ml. of 10 per cent ammonium molybdate, and 16 ml. of 5 per cent 8-hydroxyquinoline in 0.6 N hydrochloric acid.

Procedure. Heat to 70° C. 100 ml. of a neutral or slightly acid solution containing not more than 10 mg. of phosphorus pentoxide and add 30 ml. of the precipitating reagent. Allow to stand 12 hours and filter. Wash the precipitate with 1 per cent ammonium nitrate solution, dry at 105° C. for 4 hours and weigh. The precipitate contains 3.063 per cent of P_2O_5 . This method has also been investigated by Shik.²²⁷

Because of the large molecular weight of the precipitate, and the small amount of phosphorus contained in it, the above method is especially good for the determination of small quantities of phosphorus.

Matsevich²²⁸ has used a titration method for determining phosphorus in limestone.

Procedure. Dissolve 5 g. of the sample in 3 per cent hydrochloric acid, and to the resulting solution add an equal volume of a solution containing ammonium molybdate and 8-hydroxyquinoline (page 272). A yellow precipitate of $(\text{C}_9\text{H}_7\text{ON})_3 \cdot \text{H}_7[\text{PMo}_{12}\text{O}_{42}]$ is formed. This is filtered off, dissolved in a mixture of 2 volumes of ethyl alcohol and 3 volumes of 4 N hydrochloric acid,

and then treated with an excess of standard potassium bromate-potassium bromide solution. Next add potassium iodide solution, and titrate the liberated iodine with sodium thiosulfate (page 272). This method is sensitive and very accurate.

A similar procedure has been used by Zhukovskaya and co-workers^{229,303} for determining phosphorus in cast iron and steel. This method can be used in the presence of silica and arsenic with an accuracy of ± 0.002 per cent as compared with the gravimetric molybdate method.

Panfilov²⁸⁰ has applied the 8-hydroxyquinoline-ammonium molybdate method to the determination of P_2O_5 in plants, and reports values somewhat higher than those obtained by the standard method of Lorentz, in which the phosphorus is weighed as ammonium phosphomolybdate.

Bucherer and Meier²⁸¹ have attempted a titration method for phosphorus with ammonium molybdate in which the end point is determined by filtering and testing the filtrate for completeness of precipitation with more reagent. Results are not satisfactory with ammonium molybdate alone, but by using a mixture of ammonium molybdate and 8-hydroxyquinoline excellent results are obtained. This method has been applied to the analysis of commercial fertilizers.

Reagents. (a) Standard solution of phosphoric acid containing 0.6 g. per ml. (analyze in the usual manner).

(b) Dissolve 6 g. of 8-hydroxyquinoline in 10 ml. of concentrated hydrochloric acid and dilute to 1 liter. Five ml. of this solution is equivalent to 4.36 mg. of P_2O_5 .

(c) Dissolve 10 g. of ammonium molybdate $((NH_4)_6MoO_7O_{24} \cdot 7H_2O)$ in 100 ml. of water.

Procedure. *Standardization of the 8-hydroxyquinoline solution:* Dilute 10 ml. of concentrated hydrochloric acid somewhat and add 10 ml. of the molybdate solution. To this mixture add 5-10 ml. of the 8-hydroxyquinoline solution from a buret and dilute to 100 ml. Heat to 60-65° C. and add the standard phosphate solution from a buret, while shaking vigorously. Near the end point, filter off a little of the solution and test the filtrate with a drop of phosphoric acid solution. If 8-hydroxyquinoline is still in excess, a turbidity will appear on gentle heating, although this usually dissolves at 70° C. From the volume of phosphoric acid solution used, and from the quantity of 8-hydroxyquinoline reagent titrated, calculate the P_2O_5 equivalent of the hydroxyquinoline solution.

Determination: Make a preliminary test to determine approximately how much of the reagent is required for the titration. If more than 9 mg. of P_2O_5 is present in 20 ml. of solution, at least 10 ml. of 8-hydroxyquinoline solution should be used at the start of the titration. If the solution of phosphoric acid is so concentrated that less than 15 ml. will be required for the determination, it should be diluted to suitable strength. If the phosphoric acid content is very low, it is well to add a little of the standard solution of phosphoric acid to obtain a good precipitation.

The actual titration is carried out in the manner described for the standardization of the reagent.

The above method is satisfactory for determining 1-24 mg. of P_2O_5 . Fluorides must be absent, since they delay formation of the precipitate and thus cause error.²³²

Several important separations involving phosphorus can be effected by using 8-hydroxyquinoline. Metals such as aluminum, iron, zinc and molybdenum can be removed from solutions of phosphates by precipitation as the hydroxyquinolates. The phosphate remaining in the solution can be determined by means of ammonium molybdate in the usual manner.^{185,233}

Determination of silica. A crystalline, orange-colored precipitate is formed by the action of an hydrochloric acid solution of 8-hydroxyquinoline upon an acid solution of silica which has previously been treated with ammonium molybdate. The precipitate contains 12 parts of molybdic oxide (MoO_3) and 4 parts of 8-hydroxyquinoline to 1 part of silica. According to Volinetz,²³⁴ 0.1 mg. of SiO_2 per 100 ml. of solution can be precipitated by this method.

A titrimetric method by Merz²³⁵ depends on the formation of the above precipitate with 8-hydroxyquinoline and ammonium molybdate, followed by the bromination of the excess 8-hydroxyquinoline with an excess of potassium bromate-potassium bromide, and the titration of the excess bromate iodometrically. The value of the bromate solution in terms of silica is determined empirically. Vasil'ev and Barinova²³⁶ have used a similar method for determining silicic acid in aluminate solutions containing chromium and fluorides.

The method of Berg and Teitelbaum²³⁷ for determining silica by titrating the precipitate of 8-hydroxyquinoline silicomolybdate with potassium bromate-potassium bromide, and back-titrating with sodium thiosulfate has been used with good results by Volinetz^{238,239} for determining silica in minerals, and by Ginsburg²⁴⁰ for determining silica in lead and copper slags.

Determination of germanium. Germanium may be precipitated with 8-hydroxyquinoline and ammonium molybdate as hydroxyquinoline germanomolybdate. This precipitate may be weighed or titrated bromimetrically for the estimation of germanium. The following method is described by Alimarin and Alekseeva:²⁴¹

Reagent. Dissolve 20 g. of 8-hydroxyquinoline in 120 ml. of concentrated acetic acid and dilute to 1 liter.

Wash solution. Mix 7 ml. of concentrated hydrochloric acid with 25 ml. of the reagent solution and dilute to 1 liter with water.

Procedure. To 50 ml. of the neutral or slightly acid solution of a germanate, add 2 ml. of a 5 per cent, freshly prepared solution of ammonium molybdate, and 3 ml. of 10 per cent sulfuric acid. Dilute with water to 100 ml. and let stand 5 minutes. Add 9 ml. of concentrated hydrochloric acid, and then add slowly and with vigorous stirring 20 ml. of the reagent. Allow to stand 3 hours at room temperature (overnight if the germanium content is low). Filter through a weighed porous glass crucible, and wash the precipitate with the wash solution. Dry at $110^\circ C.$ and weigh. From the weight of the 8-hydroxyquinoline complex, subtract the weight of the residue obtained in

a blank experiment, and multiply by the factor 0.0448 for germanic oxide or 0.0311 for germanium.

The precipitate may be determined titrimetrically by the method of Berg.

Alkali metals. Sue²⁴² has studied the hydroxyquinolates of lithium, sodium, potassium, and ammonium, and has found that they are too soluble to be of analytical value.

Detection of arsenic. 8-Hydroxyquinoline reacts with arsenite to form a yellow precipitate, which is soluble in alcohol, and which yields a greenish blue color with ferric chloride.²⁸¹

Determination of ruthenium. 8-Hydroxyquinoline yields a green coloration with trivalent ruthenium in an acetate medium. The hydroxyquinolate can be extracted with chloroform.

Separation of beryllium. Fresenius and Frommes¹⁴⁵ describe a method for the precipitation of iron, aluminum, copper, molybdenum, and nickel in the procedure for the determination of beryllium in steel. A similar procedure has been used for the separation of iron and beryllium in the analysis of minerals.¹⁴¹ Niessner¹⁴⁶ has made use of the fact that with suitable conditions beryllium does not precipitate with 8-hydroxyquinoline, while aluminum, iron, and copper are precipitated. Hackl¹⁴⁷ has studied the effect of the presence of chromium on this separation, and finds a more or less complete precipitation of chromium occurs. Churchill, Bridges, and Lee²⁴⁸ have studied the use of 8-hydroxyquinoline in the determination of beryllium in aluminum.

Separation of lithium from aluminum, iron, and magnesium. Aluminum, magnesium, and iron may be separated from lithium in the analysis of aluminum-lithium alloys by first removing most of the aluminum by saturating the chloride solution with hydrochloric acid and, after filtration and removal of silica, treating with ammonium hydroxide and precipitating the residual aluminum, iron, and magnesium with 8-hydroxyquinoline.²⁴³

Detection of rhenium. The crystals obtained with 8-hydroxyquinoline and the chlororhenic acid, H_2ReCl_6 , may be used for the identification of the latter.^{244,274} 8-Hydroxyquinoline may also be used to distinguish between the two chlororhenic acids, HReCl_4 and H_2ReCl_6 .

Fluorescence analysis. Goto²⁴⁵⁻²⁴⁷ has detected aluminum, zinc, calcium, cadmium, magnesium, beryllium and zirconium by means of the fluorescence of their hydroxyquinolates. These reactions are as follows:

Cadmium: The precipitate of cadmium hydroxyquinolate shows a strong yellow fluorescence. As little as 0.1 γ of Cd gives this test. Several ions interfere.

Aluminum: The aluminum compound, like that of cadmium, gives a strong yellow fluorescence with only 0.1 γ of Al.

Zinc: Zinc behaves like cadmium.

Calcium: Calcium can be detected by the fluorescence of the hydroxyquinolate in the presence of ammonia. As little as 0.15 γ of calcium can be detected, but filter paper often contains enough calcium to give this test.

Magnesium: The strong fluorescence of magnesium hydroxyquinolate serves to detect as little as 0.025 γ of Mg.

Beryllium: Beryllium hydroxyquinolate in a neutral solution forms with only 0.05 γ of Be.

Zirconium: Zirconium behaves like cadmium. As little as 0.5 γ of Zr gives the test.

Chromatographic analysis using 8-hydroxyquinoline. Erlenmeyer and Dahn²⁴⁹ have used 8-hydroxyquinoline as the adsorption agent in the chromatographic analysis of several ions. In their experiments, they placed the reagent in a tube 5-8 cm. in length and 0.3 cm. in diameter. Adsorption is due to the formation of hydroxyquinolates. The order in which adsorption takes place, and the color of the layers formed is as follows:

- | | | |
|-----|------------------------------|--|
| (1) | VO ₃ ⁻ | grayish-black |
| (2) | WO ₄ ⁼ | yellow |
| (3) | Cu ⁺⁺ | green |
| (4) | Bi ⁺⁺⁺ | yellow |
| (5) | Ni ⁺⁺ | green |
| (6) | Co ⁺⁺ | pink |
| (7) | Zn ⁺⁺ | yellow with intense green fluorescence |
| (8) | Fe ⁺⁺⁺ | black |
| (9) | UO ₃ ⁼ | reddish-orange |

The order of adsorption seems to correspond rather well to the order of solubility of the hydroxyquinolates, but it also depends somewhat on the pH of the liquid. For example, the order of zinc and iron is reversed in acetic acid solutions. The sensitivities also vary with the color formed. This method is satisfactory for qualitative or semi-quantitative tests.

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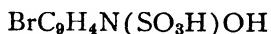
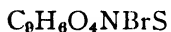
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7-BROMO-8-HYDROXYQUINOLINE-5-SULFONIC ACID



Mol. Wt. 304.12

Use: Detection and determination of copper, iron and titanium.

7-Bromo-8-hydroxyquinoline-5-sulfonic acid is a crystalline solid containing 1 mole of water of hydration. It is soluble in alcohol and decomposes without melting at 280° C.

Preparation: 7-Bromo-8-hydroxyquinoline-5-sulfonic acid is prepared by gradually adding 1 mole of bromine to 1 mole of 8-hydroxyquinoline-5-sulfonic acid.^{1,2}

Reactions. 7-Bromo-8-hydroxyquinoline-5-sulfonic acid reacts with metals in a manner similar to 8-hydroxyquinoline-5-sulfonic acid and may be used like this compound or 8-hydroxyquinoline in the detection and determination of such metals as iron, copper and titanium.^{3,4,5}

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5,7-DIBROMO-8-HYDROXYQUINOLINE

Synonym: Bromoxine



Mol. Wt. 302.97

Beil. Ref. XXI, 97 (222)



Use: Detection of copper, iron, titanium and vanadium. Determination of aluminum, cobalt, copper, gallium, iron, lead, titanium and zirconium.

Bromoxine is obtained as needle-like crystals by crystallizing from alcohol. It melts at 196° C. It is insoluble in cold water, slightly soluble in ether, and readily soluble in chloroform, alcohol, acetic acid, and benzene. It is insoluble in dilute acids.

Preparation: Dissolve 20 g. of 8-hydroxyquinoline in pure chloroform with cooling in ice. Separately dissolve a little less than the equivalent quantity of bromine in cold chloroform, and add this solution dropwise to the solution of 8-hydroxyquinoline with continuous shaking. As soon as the yellow precipitate has settled, and the supernatant liquid is a pale yellow, add more bromine from a pipet until the dibromo substitution product is formed, and a slight excess of bromine is shown by the color of the chloroform solution. Filter, and wash on a suction plate with cold chloroform until the excess of bromine has been

removed. Dry with suction, and extract with alcohol in a Soxhlet extractor. Recrystallize the product from hot benzene until the crystals are almost colorless and the benzene is entirely colorless.¹

The 5,7-dibromo derivative of 8-hydroxyquinoline, possesses the same reactive grouping as 8-hydroxyquinoline, and consequently exhibits many of the analytical characteristics of the latter. It reacts with solutions of metallic ions to form complexes of the same type as those with 8-hydroxyquinoline.

Separation and determination of copper, titanium, iron, and aluminum. In a solution of pH 1.3-1.9 bromoxine forms a greenish-yellow precipitate with cupric copper; a greenish-black precipitate with ferric iron; and a brownish-yellow precipitate with titanium. A precipitate is obtained with a solution containing 0.4 mg. of ferric ion in 200 ml., and with solutions of titanium and copper containing only 0.2 mg. of the ion in 200 ml. The copper precipitate contains 9.53 per cent copper; the iron precipitate 5.81 per cent iron; and the titanium precipitate 7.17 per cent titanium.^{2,3,4}

The following method for determining titanium, copper, or iron has been used by Berg and Küstenmacher:^{5,6}

Reagent. Dissolve 30-35 mg. of bromoxine in 100 ml. of 20-30 per cent acetone containing sufficient hydrochloric or nitric acid to make the solution 0.05-0.025 N in acid.

Procedure. Heat the solution containing the metallic ion to 50° C. and add the necessary volume of reagent (3 ml. for each mg. of copper, 7 ml. for each mg. of iron, and 5 ml. for each mg. of titanium) dropwise with stirring. Heat to boiling and filter. Wash, first with a solution which is 0.04 N with acid and contains 10-20 per cent acetone, and finally with hot water. Dry at 120-140° C. and weigh. The factor for copper is 0.0953; for iron 0.0581; and titanium 0.0717.

In the presence of aluminum, chromium, and mercury, the acidity should be 0.20-0.25 N, and a little more reagent should be used. By adding 20 ml. of saturated ammonium oxalate to 200 ml. of solution to be analyzed, the copper salt alone is formed. In this way copper can be separated from titanium and iron.

Iron and titanium can be separated as follows:

Procedure. To the neutral solution to be analyzed, add 2 g. of tartaric acid or 3 g. of ammonium tartrate and 2 g. of malonic acid. Then after adding a little acetone, dilute to 100 ml., add 10 ml. of N hydrochloric acid. Precipitate iron in the usual manner. Titanium remains in solution.

Dubsky and Chytil⁷ prefer the method of Hasse¹ for the determination of copper, although Hecht and Reissner⁸ recommend that of Berg and Küstenmacher.⁵ The latter method appears to be superior to those using benzoinoxime or salicylaldoxime.

Hasse's method¹ is particularly well suited to the determination of copper in water which has been treated with a copper salt for algae:

Reagent. Dissolve to 0.5 g. of bromoxine in 100 ml. of 5 N hydrochloric acid.

Procedure. To 200 ml. of the water to be analyzed, add 1 ml. of N hydrochloric acid and about 10 drops of perhydrol. Boil until the solution is colorless. Filter, add 2 ml. of the reagent (suitable for 5-10 mg. of copper), and again filter after the precipitate has formed. Dry the precipitate for 1 hour at 105° C. and for 2 hours at 150° C. Heating at 150° volatilizes the excess reagent. The precipitate is $(C_6H_4ONBr_2)_2Cu$. The factor for copper is 0.0953.

Zan'ko and Bursuk^{9,10} have adapted the method of Berg to the determination of copper in cast iron and steel. The method is accurate to 0.004-0.04 per cent for 0.07-2 per cent copper content.

Procedure. Decompose 0.5-1.0 g. of sample in 15 ml. of 50 per cent hydrochloric acid. Oxidize with 2 ml. of nitric acid, and evaporate the solution to dryness. Heat the residue in a drying oven at 120-130° C., and dissolve in hydrochloric acid and water. Filter from insoluble silica. Decompose the silica with sulfuric acid and hydrofluoric acid in the usual manner, and dissolve the residue in water. Filter, and unite the two filtrates, and then dilute to 100 ml. Add 15 g. ammonium oxalate and heat, and neutralize with ammonium hydroxide to nitrazine-yellow paper by a spot test. Treat the solution with 15-20 ml. of N hydrochloric acid and 10-15 ml. of acetone. Heat to 60° C. and add dropwise, with shaking, 0.5 per cent bromoxine reagent in acetone in excess (not exceeding 0.05-0.08 g.). Digest on a water bath for 2-3 minutes and filter. Wash the precipitate with 100 ml. of water containing 0.5 g. ammonium oxalate, 4.0 ml. of 0.1 N hydrochloric acid and 10 ml. of acetone, and finally wash 10-12 times with hot water. Dry the precipitate in a Gooch crucible in an oven at 160° and then at 190°. Weigh and determine as $(C_6H_4Br_2NO)_2Cu$. The factor for copper is 0.0953.

Ishimaru¹¹ has studied the drying temperatures of the salts of bromoxine and recommends those given in Table 47.

TABLE 47.

Metal	Formula of Precipitate	Proper Drying Temperature
Titanium	$TiO(C_6H_4Br_2ON)_2$	116-117°
Iron	$Fe(C_6H_4Br_2ON)_2$	118-140°
Copper	$Cu(C_6H_4Br_2ON)_2$	127-177°

The determination of titanium as $TiO(C_6H_4Br_2ON)_2$ by drying cannot be recommended, since the proper drying range is very small.

The above metals may be determined by mixing anhydrous oxalic acid with the precipitate formed with bromoxine, and igniting to the oxide. The proper ignition temperatures given by Ishimaru are shown in Table 48.

TABLE 48.

Metal	Oxide	Proper Ignition Temperature
Titanium	TiO ₂	>400°
Iron	Fe ₂ O ₃	>458°
Copper	CuO	>525°

Zan'ko and Bursuk¹² have proposed an interesting method for determining iron, titanium, and aluminum in a mixture. This determination depends on the separation of iron with 8-hydroxyquinoline, and by the precipitation of aluminum and titanium at different acidities with bromoxine, which is formed directly in the filtrate by bromination of 8-hydroxyquinoline. For the details of this method, see the section on 8-hydroxyquinoline (page 291).

Determination of iron. An aqueous solution of 5,7-dibromo-8-hydroxyquinoline cannot be used for the colorimetric determination of iron due to the insolubility of the reagent in water and hydrolysis of the iron complex. An acetone solution of the reagent, however, yields a deep green color with ferric iron. This reagent may be used advantageously in the colorimetric determination of iron, since the ferric complex is soluble in ether, chloroform and carbon tetrachloride. Thus, small quantities of iron may be extracted from aqueous solutions and the sensitivity of the reaction increased.^{13,14}

Detection of copper, titanium, and iron. The reactions of bromoxine with solutions of copper, ferric and titanium salts may be used for the detection of these metals. The reactions are sensitive to 1 part of copper or titanium in 1 million, and 2 parts of iron in 1 million.^{6,15}

Determination of lead. Lead may be determined by the following method:¹⁶

Reagent. Dissolve 0.5 g. of bromoxine in 100 g. of 5 N hydrochloric acid.

Procedure. Make the solution to be analyzed (containing lead nitrate) slightly alkaline with ammonium hydroxide, add a little tartaric acid, and 10 per cent of acetone. Heat to 55-60° C. and add the bromoxine reagent dropwise with constant stirring. Heat on a water bath and filter the yellow precipitate. Wash with warm water containing a few ml. of acetone, and then with pure warm water. Dry at a gradually increasing temperature (up to 195°-215° C.). The precipitate contains 25.55 per cent lead.

If copper is present, lead is determined by an indirect method: determine copper by Berg's method in an acid solution, and then determine lead and copper together by the above method; the amount of lead is found by difference.

Detection of vanadium. Bromoxine yields difficultly soluble compounds with molybdates, tungstates, and salts of trivalent vanadium.¹⁷ In a solution

containing 20 per cent nitric acid the reagent reacts only with ferric iron and trivalent vanadium, forming green and brown precipitates respectively. Iron may be removed prior to making the vanadium test by precipitating as ferric hydroxide with sodium hydroxide.

Procedure. In the absence of iron, place 0.3 ml. of solution to be tested in a dish and add 0.5 ml. of a saturated alcoholic solution of the reagent. A brown precipitate or color indicates trivalent vanadium.

If iron is present, treat the solution to be tested dropwise with 3 N sodium hydroxide to precipitate ferric hydroxide. Boil and filter. Acidify the filtrate with nitric acid and make the test as described above. Under these conditions molybdates cause a change of color to a canary yellow. As little as 30 γ of vanadium can be detected at a dilution of 1/10,000.

Determination of zirconium. Bromoxine forms an insoluble zirconium salt, but this reaction is of no great value in analytical chemistry because it is very difficult to separate zirconium from the reagent.¹⁸

Determination of cobalt. Ablov¹⁹ has prepared the cobalt derivative of bromoxime, but this compound has not been used to advantage in an analytical procedure.

Separation and determination of gallium. Bromoxine may be used for a simple and satisfactory separation of gallium and aluminum.²⁰ Gallium is precipitated by the reagent in a dilute mineral acid solution containing acetone. Aluminum is not precipitated under these conditions. Precipitation of gallium is best carried out in a boiling solution, acidified with hydrochloric acid, by adding an excess of a cold saturated solution of the reagent in acetone. The solution should be about 0.06 N in hydrochloric acid, and should contain 30 per cent acetone by volume. The precipitate corresponds to the formula $\text{Ga}(\text{C}_6\text{H}_4\text{Br}_2\text{NO})_3$. It can be ignited with oxalic acid to Ga_2O_3 . The concentration of the gallium solution should not exceed 0.03 mg. gallium per ml. Iron and gallium behave similarly.

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2. W. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934).
3. E. Hertel and H. Kleu, *Ber.* **61**, 1653-54 (1928); *C.A.* **23**, 51 (1929).
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5. R. Berg and H. Küstenmacher, *Z. anorg. allgem. Chem.* **204**, 215-21 (1932); *C.A.* **26**, 2135 (1932).
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9. A. M. Zan'ko and A. Bursuk, *Zavodskaya Lab.* **6**, 675-8 (1937); *C.A.* **31**, 8424 (1937).
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13. J. Molland, *Tids. Kjemi Bergvesen Met.* **1**, 49-52 (1941).

14. J. Molland, *Arch. Math. Naturvidenskab*, **43**, 67-184 (1940).
15. R. Berg, *Z. anal. Chem.* **70**, 341-7 (1927); *C.A.* **21**, 1778 (1927).
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17. G. Gutzeit and Monnier, *Helv. Chim. Acta*, **16**, 239-40 (1933); *C.A.* **27**, 2649 (1933).
18. P. Sue and G. Wetroff, *Bull. soc. chim.* [5] **2**, 1002-07 (1935); *C.A.* **29**, 5844 (1935).
19. A. Ablov, *Bul. soc. chim.* [4] **53**, 234 (1931); *C.A.* **27**, 3892 (1933).
20. E. Gastinger, *Z. anal. Chem.* **126**, 373-82 (1944); *C.A.* **38**, 5466 (1944).

5,7-DICHLORO-8-HYDROXYQUINOLINE

Synonym: Chloroxine



Mol. Wt. 214.05

Beil. Ref. XXI, 95 (222)

**Uses:** Determination of copper, iron and titanium.

This compound is obtained as needle-like crystals from alcohol. It melts at 179-80° C. It is soluble in benzin, benzene, and acetone, and it is slightly soluble in cold alcohol and acetic acid. It also dissolves readily in sodium and potassium hydroxides and in acids to form yellow solutions.

Preparation: Pass a stream of chlorine through 10 per cent solution of 8-hydroxyquinoline in acetic acid until the dark brown solution turns wine-yellow and green flocks begin to separate. At this point the chlorination is interrupted and the mixture poured into water. The crystals which separate are recrystallized several times from alcohol.¹

5,7-Dichloro-8-hydroxyquinoline possesses the same reactive group as 8-hydroxyquinoline and forms similar complex salts (page 265). Because of this similarity in structure 5,7-dichloro-8-hydroxyquinoline resembles 8-hydroxyquinoline in many of its analytical reactions.

Determination of copper, iron and titanium. Fresenius² has suggested the use of 5,7-dichloro-8-hydroxyquinoline as a satisfactory reagent for the determination of copper, iron and titanium. These metals are quantitatively precipitated with the reagent, and the precipitates may be weighed after drying.^{2,3,4}

Procedure. To 200 ml. of solution containing the metal to be determined, add mineral acid until the acidity is 0.2 N (0.1 N for titanous acid), and heat to 50° C. Add dropwise with constant stirring a 1-2 per cent acetone solution of the reagent. Add the reagent in slight excess. Heat to boiling for 5 minutes, and filter while hot through a glass filter crucible. Wash with a warm 25 per cent acetone solution 0.04 N with mineral acid, and finally with pure hot water. Dry at 120-140° C. to constant weight and weigh.

With copper a green precipitate containing 13 per cent copper is obtained. The iron precipitate is black-green and contains 8.03 per cent iron, while the titanium precipitate is orange-brown in color and contains 9.82 per cent of titanium.

Ishimaru⁵ has studied the drying temperatures of the precipitates formed when 5,7-dichloro-8-hydroxyquinoline reacts with metallic ions, and recommends those given in Table 49. These metals can be determined after precipitation by mixing the precipitate with anhydrous oxalic acid and igniting to the oxide. The proper ignition temperatures recommended by Ishimaru are given in Table 50.

TABLE 49.

Metal	Formula	Drying Temperature
Titanium	$\text{TiO}(\text{C}_6\text{H}_4\text{Cl}_2\text{ON})_2$	142-169°
Iron	$\text{Fe}(\text{C}_6\text{H}_4\text{Cl}_2\text{ON})_3$	112-198°
Copper	$\text{Cu}(\text{C}_6\text{H}_4\text{Cl}_2\text{ON})_2$	122-192°

TABLE 50.

Metal	Oxide	Proper Ignition Temperature
Titanium	TiO_2	>443°
Iron	Fe_2O_3	>478°
Copper	CuO	>525°

Molland^{6,7} has studied the use of 5,7-dichloro-8-hydroxyquinoline as a reagent for the colorimetric determination of iron. An aqueous solution of the reagent gives no color with iron due to the small solubility in water. A green color is obtained, however, if the reagent is dissolved in acetone or alcohol. The reagent is inferior for the iron determination, but does possess the advantage that the iron complex can be extracted with ether or chloroform.

1. A. Hebebrand, *Ber.* **21**, 2980 (1888).
2. W. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934); *C.A.* **28**, 3683 (1934).
3. E. Hertel and H. Kleu, *Ber.* **61**, 1653-54 (1928); *C.A.* **23**, 51 (1929).
4. R. Berg, *Z. anorg. allgem. Chem.* **204**, 208 (1932).
5. S. Ishimaru, *J. Chem. Soc. Japan.* **55**, 201-12 (1934); *C.A.* **28**, 3681 (1934).
6. J. Molland, *Tids. Kjem. Bergvesen Met.* **1**, 49-52 (1941).
7. J. Molland, *Arch. Math. Naturvidenskab.* **43**, 67-184 (1940).

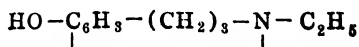
N-ETHYL-8-HYDROXYTETRAHYDROQUINOLINE HYDROCHLORIDE

Synonym: Karin A

$\text{C}_{11}\text{H}_{15}\text{ON}$

Mol. Wt. 177.23

Beil. Ref. XXI, 64.



Use: Detection of arsenic.

Karin A is obtained as white crystals from water. It is easily soluble in water, but is only slightly soluble in hydrochloric acid.

Preparation: *8-Hydroxytetrahydroquinoline*: Heat 8-hydroxyquinoline with tin and hydrochloric acid on a water bath for about 1 hour. Pour off the solution from the tin and concentrate on a water bath. Upon cooling a double salt of 8-hydroxytetrahydroquinoline and stannous chloride separates. Remove most of the hydrochloric acid by evaporation and precipitate tin with hydrogen sulfide. Filter, concentrate the filtrate, and make alkaline with sodium carbonate. Extract the mixture with ether, and recover 8-hydroxytetrahydroquinoline by evaporating the ether. Purify the product by recrystallization from benzene (M.P. = 121-122° C.).¹

N-ethyl-8-hydroxytetrahydroquinoline hydrochloride: Mix 1 mole of 8-hydroxytetrahydroquinoline with 1 mole of ethyl iodide and heat to 50-60° C., or with 1 mole of ethyl bromide in a tube at 120° C. Cool, dissolve the product in water, and precipitate the free base with sodium carbonate. Filter quickly, wash with water and crystallize from ether. Convert to the hydrochloride with hydrochloric acid.²

Detection of arsenic. Reppmann³ recommends the use of Karin A for the detection of small quantities of arsenic.

Procedure. Place a drop of a solution containing arsenic as arsenite on a strip of filter paper and moisten with a drop of concentrated hydrochloric acid. Add a drop of a 0.5 per cent aqueous solution of the reagent and 1 drop of a 1 per cent solution of ferric chloride. Warm the test paper carefully. A reddish-brown coloration appears if arsenic is present. With this reaction as little as 0.0006γ of arsenic can be detected at a concentration of only 0.1γ per ml.

Mercury, lead and copper interfere. Calcium, strontium, barium, aluminum, chromium, cobalt, nickel, bismuth, antimony and arsenates do not.

Arsenic can be detected in organic matter by first treating with hydrogen peroxide in the presence of concentrated sulfuric acid and then reducing the arsenate to arsenite by means of hydrazine sulfate.

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3. W. Reppmann, *Z. anal. Chem.* **99**, 180-82 (1934); *C.A.* **29**, 5037 (1935).

8-HYDROXYQUINALDINE Synonym: 2-Methyl-8-hydroxyquinoline

$C_{10}H_9NO$

Mol. Wt. 159.17

Beil. Ref. XXI, 106.

$CH_3-C_9H_8N-OH$

Use: Determination of aluminum, magnesium and zinc.

8-Hydroxyquinaldine is obtained as prisms from alcohol. It melts at 74° C. and boils at 266-277° C. It is insoluble in water, but is readily soluble in hot alcohol, ether and benzene. It is soluble in dilute alkalis.

Preparation: Dissolve 55 g. of o-aminophenol and 25 g. of o-nitrophenol in 100 g. of 12 N hydrochloric acid, which is contained in a 3-necked flask. Fit

the flask with a reflux condenser, a mechanical stirrer and a dropping funnel. Now add 40 g. of crotonaldehyde with stirring over a period of 45 minutes. Heat on a water bath for 6 hours with continual stirring, and allow the mixture to stand overnight. Remove the excess *o*-nitrophenol by steam distillation from an acid solution.

Add 6 N sodium hydroxide to the residue until nearly neutralized, and then saturate with sodium carbonate and steam distill. Distill the crude product under reduced pressure (water pump), and recrystallize from an alcohol-water mixture, using 20 ml. of 95 per cent ethyl alcohol and 10 ml. of water for each 5 g. of the crude material. The reagent may be further purified by an additional crystallization.^{1,2}

Analytical reactions. In general, 8-hydroxyquinaldine is similar to 8-hydroxyquinoline in its analytical properties, but seems to be more selective in its action. It is especially noteworthy that, unlike 8-hydroxyquinoline, 8-hydroxyquinaldine does not precipitate aluminum. In acetic acid-acetate buffered solutions 8-hydroxyquinaldine forms precipitates with bismuth, cadmium, chromium, cobalt, copper, ferrous, ferric, manganese, nickel, silver, titanium (TiO^{++}), zinc, molybdate, tungstate and vanadate. It does not yield precipitates with beryllium, aluminum, calcium, strontium, barium, lead, magnesium, potassium, sodium or ammonium. Precipitates are not formed with bismuth and stannic tin in tartrate solutions.

In ammoniacal solutions, 8-hydroxyquinaldine precipitates the same ions as in acetic acid-acetate solutions, with the exception of molybdate, tungstate and small quantities of vanadate, and in addition, lead, calcium, magnesium, and strontium are precipitated. Aluminum, however, is not precipitated, although tartrate must be added to the solution to prevent precipitation of aluminum hydroxide.

Since many precipitations with 8-hydroxyquinaldine are quantitative, a number of valuable separation and determination procedures are possible.

Determination of zinc. Zinc may be separated from aluminum and magnesium by precipitating in an acetic acid-acetate buffered solution with 8-hydroxyquinaldine. Zinc is estimated, either by direct weighing of the precipitate, or by titration by bromination. If aluminum is present, tartrate must be added to prevent precipitation of basic aluminum salts.

Reagent. Dissolve 5 g. of 8-hydroxyquinaldine in 12 g. of glacial acetic acid and dilute to 100 ml. with water.

Procedure. If aluminum is present, add 1 g. of ammonium tartrate to the clear, slightly acid solution. Add 2 ml. of the 8-hydroxyquinaldine solution for each 10 mg. of zinc present, and dilute to about 200 ml. Heat the mixture to 60-80° C., and neutralize the excess acid by the dropwise addition of 1:5 ammonium hydroxide until the precipitate which forms just redissolves on stirring. Add 45 ml. of 2 N ammonium acetate slowly and with stirring. The pH of the solution should be at least 5.5. Allow the mixture to stand 10-20 minutes, and filter through a Gooch or filter crucible. If the quantity of zinc

is small, and the amount of aluminum and magnesium large, allow the solution to stand several hours before filtering. Wash the precipitate well with hot water. Dry at 130-140° C. for 2 hours and weigh as $\text{Zn}(\text{C}_{10}\text{H}_8\text{NO})_2$. The factor for zinc is 0.1713.

Zinc may be determined titrimetrically by the following method:

Procedure. Precipitate zinc as described in the above procedure, and filter through filter paper. Dissolve the washed precipitate with 30 ml. of hot 1:2 hydrochloric acid, and wash the filter thoroughly with hot 1:3 hydrochloric acid, and then with hot water. Moisten the paper with 2 drops of concentrated hydrochloric acid before the final two washings with water to insure the complete solution of the zinc complex.

If the quantity of zinc is small and the amount of aluminum and magnesium large, reprecipitate zinc as described above. Use only 1-2 ml. of the reagent for the second precipitation. Dissolve the second precipitate in 30 ml. of hot 1:3 hydrochloric acid, and wash thoroughly with hydrochloric acid and water as before. Add 3 g. of potassium bromide to the filtrate. Dilute the solution to about 150 ml., and add a few drops of methyl red indicator. Run in a standard solution of 0.1 N potassium bromate solution from a buret until an excess is indicated by the bleaching of the indicator. Add 5 ml. of the bromate solution in excess. Add 3 g. of potassium iodide, and stir until dissolved. Titrate with a standard solution of sodium thiosulfate, using a 2 per cent starch solution as indicator. One ml. of 0.1 N potassium bromate solution is equivalent to 0.8172 mg. of zinc.

Determination of magnesium. After the precipitation of zinc from an acetic acid-acetate solution with 8-hydroxyquinaldine, magnesium may be determined in the filtrate, if no aluminum is present, by increasing the pH to 9.3 or higher. In the presence of tartrates and ammonium salts, as is the case when aluminum is present, the magnesium complex precipitates so slowly as to make the method useless. Quantities of calcium exceeding 2-3 mg. interfere with the magnesium determination and should be removed.

Reagent. Dissolve 5 g. of 8-hydroxyquinaldine in 12 g. of glacial acetic acid and dilute with water to 100 ml.

Procedure. In the absence of aluminum, the filtrate from the zinc determination may be used for the determination of magnesium. Add 3 ml. of the 8-hydroxyquinaldine reagent for each 10 mg. of magnesium, and add ammonium hydroxide until the pH is 9.3, or until the precipitate no longer forms. Digest the solution at 60-80° C. for 20 minutes, and filter through a Gooch or filter crucible. Wash the precipitate with hot water, dry at 130-140° C. and weigh as $\text{Mg}(\text{C}_{10}\text{H}_8\text{NO})_2$. The factor for magnesium is 0.07139.

Zinc may be determined by a titrimetric procedure after precipitating as the 8-hydroxyquinaldinate. An alcoholic solution of the reagent must be used for the precipitation, since the reagent is more soluble in the presence of alcohol and is not coprecipitated in alkaline solutions. No difficulty is encountered in gravimetric determinations, since any coprecipitated reagent is volatile at 130° C.

The magnesium salt is soluble in hot 95 per cent alcohol, and undoubtedly the solubility in water is slightly increased by the presence of alcohol; consequently only the required quantity of the alcoholic solution should be used. In the titrimetric procedure, the magnesium precipitate is collected on paper, dissolved in hydrochloric acid, and titrated as described in the section on zinc. One ml. of 0.1 N potassium bromate is equivalent to 0.3040 mg. of magnesium.

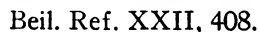
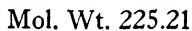
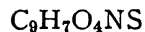
Determination of aluminum. Aluminum may be determined after the removal of zinc with 8-hydroxyquinoline, by precipitating with 8-hydroxyquinoline.

Procedure. Warm the filtrate from the zinc determination to 60-80° C., and add 40 ml. of a 2.5 per cent solution of 8-hydroxyquinoline in 7.5 per cent acetic acid, and then add 10 ml. of 2 N ammonium acetate. Allow to stand 10-20 minutes and filter through a Gooch or filter crucible. Wash with hot water and dry at 130-140° C. for at least 2 hours. Weigh as aluminum 8-hydroxyquinolate.

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2. L. L. Merritt, Jr., and J. K. Walker, *Ind. Eng. Chem., Anal. Ed.* 16, 387-9 (1944); *C.A.* 38, 3921 (1944).

8-HYDROXYQUINOLINE-5-SULFONIC ACID

Synonym: Quinosol is the potassium salt of 8-hydroxyquinoline-5-sulfonic acid



Use: Detection of bismuth, copper, iron, silver and vanadium.

Determination of bismuth, copper, iron, silver, vanadium and zinc.

Vaisman¹ has reported the use of quinosol as a reagent for the determination of zinc. This reagent is described in the literature as the potassium salt of 8-hydroxyquinoline-7-sulfonic acid. Molland² however, has investigated the structure of this compound and claims that without doubt it is the 5-sulfonic acid.

8-Hydroxyquinoline-5-sulfonic acid is a yellow crystalline powder which melts at 310-313° C. It is only very slightly soluble in alcohol and in cold water, but it is more soluble in boiling water. It is insoluble in benzene. The potassium salt is obtained as leaves on crystallizing from water.

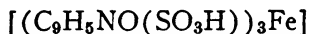
Preparation: Add 8-hydroxyquinoline in small portions to 5-6 parts of cold fuming sulfuric acid containing about 20 per cent SO_3 . Allow to stand for 24 hours at room temperature and pour the reaction mixture into 8-10 parts of ice water. The reagent separates as a yellow crystalline precipitate. Filter and recrystallize from water.²⁻⁷

8-Hydroxyquinoline-5-sulfonic acid possesses the same reactive group as 8-hydroxyquinoline and reacts similarly (page 265).

Determination of zinc. 8-Hydroxyquinoline-5-sulfonic acid forms an insoluble complex with zinc. The zinc salt $\text{Zn}(\text{C}_9\text{H}_5\text{ONSO}_3\text{H})_2$ is precipitated as an insoluble yellow powder upon the addition of the potassium salt of the reagent (quinisol) to an aqueous solution of a zinc salt. A procedure for the determination of zinc has been based upon this reaction.^{1,8,9}

Procedure. To 5-10 ml. of a 0.3 per cent solution of zinc sulfate, add 20 ml. of 1 N sodium hydroxide, 20 ml. of 20 per cent sodium tartrate, and 60-70 ml. of water. Add 10 ml. of a 2 per cent aqueous solution of the potassium salt of 8-hydroxyquinoline-5-sulfonic acid and heat to 60-70° C. Allow to stand for a few minutes and filter through moist cotton. Wash the precipitate with 1 per cent sodium tartrate solution until the filtrate passes through colorless. Transfer the filter and precipitate to a beaker and dissolve in 20-30 ml. of hot dilute hydrochloric acid. Wash the funnel with 20 ml. of water, cool and add 0.5-1.0 g. of potassium bromide and 1-2 drops of methyl red. Titrate with 0.1 N potassium bromate until the color disappears. Add 2-3 ml. of 0.1 N potassium bromate and 0.5 g. of potassium iodide, and titrate the liberated iodine with 0.1 N sodium thiosulfate, using starch as the indicator. One ml. of 0.1 N potassium bromate corresponds to 0.000817 g. of zinc or 0.00359 g. of zinc sulfate.

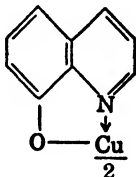
Detection and determination of iron. 8-Hydroxyquinoline-5-sulfonic acid reacts with ferric chloride to yield a deep green color.^{2,10,11} This is due to the formation of an inner-complex of the following composition:



The reaction does not occur if the solution is very acid or alkaline. The optimum pH appears to be about 4.0. Oxalic acid and other complex forming substances, such as citric, phosphoric and arsenic acids and fluorides interfere. A biphthalate buffer, however, may be used without disturbing the reaction. The color is developed in a solution that has been made neutral and mixed with an equal volume of 0.2 N potassium acid phthalate. This method is suitable for the colorimetric determination of iron in the absence of interfering substances. Copper, zinc, cadmium, mercuric, aluminum, stannic, lead, cobalt and nickel salts interfere by forming metallic complexes with the reagent. Free chlorine, bromine and hydrogen peroxide destroy the color completely. Ammonium, sodium, potassium, lithium, calcium, strontium, barium, magnesium, thallous, chromic, manganous, chloride, bromide, iodide, sulfate, nitrate, dichromate, cyanide, borate and thiocyanate ions do not interfere.

Detection and determination of vanadium. 8-Hydroxyquinoline-5-sulfonic acid reacts with a solution of metavanadate to give a permanent brown color which can be used for the detection or colorimetric estimation of vanadium.^{11,12} The determination can be carried out with an error of 2 per cent in a solution containing 0.00005 moles per liter of ammonium metavanadate or 2.55 mg. of vanadium per liter of solution.

Detection and determination of copper, bismuth and silver. A voluminous yellowish precipitate of the copper complex of 8-hydroxyquinoline-5-sulfonic acid separates from a solution containing a copper salt upon the addition of a



0.1 per cent solution of the potassium salt of 8-hydroxyquinoline-5-sulfonic acid. The mixture should be allowed to stand overnight. The precipitate is composed of a flocculent mass of bundles of delicate needles. A solution containing as little as 0.0002 per cent copper gives a distinct precipitate which may be easily collected. Other common metals do not give precipitates at high dilutions, although a precipitate is obtained from a more concentrated solution of a mercuric salt.^{2,9,10,13-15}

Bismuth is precipitated as insoluble yellow $\text{Bi}(\text{OH})_2(\text{C}_9\text{H}_5\text{ONSO}_3\text{H})$ upon the addition of the potassium salt of 8-hydroxyquinoline-5-sulfonic acid to a solution of a bismuth salt. The silver salt of 8-hydroxyquinoline-5-sulfonic acid is precipitated as a light yellow compound in a similar manner.

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6. St. Niementowski and Ed. Succharda, *Ber.* 49, 16 (1916).
7. K. Matsumura, *J. Am. Chem. Soc.* 49, 810 (1927).
8. M. Haitinger, *Mikrochemie*, 16, 321-56 (1934); *C.A.* 29, 2470 (1935).
9. H. T. Liem, *Pharm. Tijdschr. Nederland. Indie* 19, 13-16 (1942).
10. J. Molland, *J. Am. Chem. Soc.* 62, 541-2 (1940).
11. J. Molland, *Tids. Kjemi Bergvesen.* 19, 119-22 (1939); *C.A.* 34, 1932 (1940).
12. J. Molland, *Compt. rend.* 210, 144-6 (1940); *C.A.* 34, 1934 (1940).
13. J. E. Saul and D. Crawford, *Analyst.* 43, 348 (1918).
14. N. Schoorl, *Pharm. Weekblad.* 56, 325 (1919).
15. L. H. Lampitt, E. B. Hughes, P. Bilham and C. H. F. Fuller, *Analyst.* 51, 327 (1926).

8-HYDROXYQUINOLINE-7-SULFONIC ACID

Use: Determination of zinc.

Determination of zinc. Vaisman¹ has reported the use of quinosol for the determination of zinc. This substance is described as the potassium salt of 8-hydroxyquinoline-7-sulfonic acid. Molland,² however, has studied this compound, and reports that it is undoubtedly the 5-sulfonic acid instead of the 7-compound as originally supposed. Consequently a description of what has been

described as 8-hydroxyquinoline-7-sulfonic acid is included under the discussion of 8-hydroxyquinoline-5-sulfonic acid.

1. G. A. Vaisman, *Ukrain. Gosudarst. Inst. Eksptl. Farm. (Kharkov.) Konsul'tatsionnye Materialy*, 143-4 (1940); *C.A.* 36, 3117 (1942).
2. J. Molland, *Arch. Math. Naturvidenskab.* 43, 67-183 (1940).

7-iodo-8-hydroxyquinoline-5-sulfonic acid

Synonym: Ferron, loretin, yatren

$C_9H_6O_4NIS$

Mol. Wt. 351.13 Beil. Ref. XXII, 408(620).

$HO_3S-C_9H_4NI(OH)$

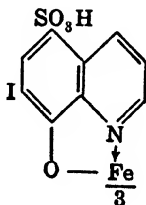
Use: Detection of barium, calcium, iron, strontium, and zinc.

Determination of calcium, fluoride and iron.

7-Iodo-8-hydroxyquinoline-5-sulfonic acid is a pale yellow almost odorless and tasteless crystalline solid. It melts at 260-270° C. with decomposition. It is only slightly soluble in water and in alcohol, and is insoluble in ether.

Preparation: Mix 40 g. of 8-hydroxyquinoline-5-sulfonic acid (crystalline, dried at 98° C. and containing 1 mole of water) with 12 g. of pure potassium carbonate and 350-400 ml. of water. Heat until a dark yellow solution is formed, and add 27.5 g. of potassium iodide in a concentrated aqueous solution. Then add in 4-5 portions 46.8 g. of bleaching powder, containing 25 per cent of active chlorine, with vigorous shaking and with continuous boiling over a free flame. Continue boiling for 15-20 minutes and allow to cool. Wash out the thick yellow paste with the least possible quantity of water into a large porcelain dish which is cooled in an ice-salt mixture. While keeping cool, and with continuous stirring, the iodination is carried out by first adding 100 ml. of dilute hydrochloric acid ($d = 1.025$) and then 45 ml. of concentrated hydrochloric acid. Filter, wash, and purify the product by recrystallization.^{1,2,3}

Detection and determination of iron. The bright yellow solution, prepared by dissolving 7-iodo-8-hydroxyquinoline sulfonic acid in water, reacts with a faintly acid solution containing ferric ions to yield a blue to green color. This color is suitable for detecting ferric iron in the presence of ferrous iron, or for the colorimetric determination of iron.⁴⁻⁶ The composition of the colored compound is shown by the following formula:



The depth of color obtained in this reaction is proportional to the concentration of ferric iron and consequently is well suited for the colorimetric determination

of iron. As little as 1 part of ferric iron in 10,000,000 parts of solution can be detected by this reaction.

The color is stable to light and does not fade on standing, but it is destroyed by strong acids or strong bases. The following procedure for determining small quantities of iron is given by Yoe.⁷

Procedure. Place a measured quantity of solution to be analyzed in a 50-ml. Nessler tube and dilute to 5 ml., and then make just acid to methyl orange paper with dilute sulfuric acid. Add 5 drops of a 0.2 per cent aqueous solution of 7-iodo-8-hydroxyquinoline sulfonic acid. Shake gently and dilute to the mark. Mix thoroughly and compare the resulting color with that of series of standards similarly prepared.

Cupric ions and salts that hydrolyze readily interfere with the above procedure and should be present, if at all, only in low concentrations. The results obtained with many different classes of materials agree for the most part with those certified by the U. S. Bureau of Standards.⁶

7-Iodo-8-hydroxyquinoline sulfonic acid may be used as a reagent for the detection or determination of iron in the presence of many cations. Among the ions which do not give reactions with the reagent are lithium, sodium potassium, rubidium, cesium, cupric, silver, auric, calcium, strontium, barium, beryllium, magnesium, zinc, cadmium, mercury, aluminum, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium, thulium, ytterbium, gallium, indium, thallium, titanium, zirconium, hafnium, thorium, germanium, tin, lead, vanadyl, columbium, tantalum, antimony, bismuth, chromium, molybdenum, uranyl, manganese, rhodium, ferrous, cobalt, nickel, ruthenium, palladium, iridium and platinum. Among the anions which do not give color reactions are borate, phosphate, arsenite, tungstate, sulfide, selenium, tellurium, fluoride, chloride, bromide and iodide.

7-Iodo-8-hydroxyquinoline sulfonic acid may thus be regarded as a specific reagent for ferric iron in the sense that no other ion appears to give a green color, but it is not to be regarded as specific in the sense that its use is free from interference by other ions.

In a recent study, Urbanyi⁸ found that both ferrous and ferric iron in low concentrations react to form the same colored product with 7-iodo-8-hydroxyquinoline-5-sulfonic acid owing to autooxidation of ferrous iron. Thus it is possible to determine small amounts of iron without previous oxidation if the total iron content of the solution does not exceed 0.06 per cent and if the mineral acid concentration is not greater than 0.1 N. Results agreeing within 1-2 per cent are obtained if a 10 per cent sodium acetate solution containing 0.3 per cent of reagent and a photocolormeter are used.

The method of Yoe possesses a number of advantages over other colorimetric methods, but it requires a much more careful control of experimental conditions than other methods such as that based upon the use of thioglycolic acid. The color of the iron-7-iodo-8-hydroxyquinoline sulfonic acid compound depends upon the concentration of the reagent as well as on the pH of the solution. A pH of 2-3 is suitable for the determination, but it is important to keep this value

constant in any series of measurements if the results are expected to agree within 2 per cent of the actual value.⁴

The following method, described by Clark and Sieling⁹ has been used for the determination of iron in humates:

Procedure. Destroy organic matter by oxidation with 30 per cent hydrogen peroxide and 10 per cent sulfuric acid. Dilute the resulting mixture to a definite volume, and to an aliquot part of the solution, add 0.1 N potassium hydroxide until a pH of 2.7-3.2 is indicated with bromophenol blue internal indicator. To a fresh aliquot, add the same quantity of 0.1 N potassium hydroxide required to give a pH of 2.7-3.2 (as indicated in the above test), and dilute the mixture to 100 ml. in a Nessler tube. Add 1 ml. of a 0.2 per cent aqueous solution of the reagent, and compare the resulting color with that of standards similarly treated. Results obtained with this method appear to be accurate to 0.001 mg. of iron.

Thiel and van Henger⁵ have used 7-iodo-8-hydroxyquinoline sulfonic acid for determining iron by a process of absolute colorimetry, although better results are claimed with dipyridyl. Pfeiffer¹⁰ reports that 7-iodo-8-hydroxyquinoline sulfonic acid cannot be used satisfactorily for the determination of iron in chromium baths.

Determination of fluorides. As described above, 7-iodo-8-hydroxyquinoline sulfonic acid reacts with slightly acid solutions of ferric salts to yield a green color, but if fluorides are present such solutions assume a yellowish hue. By matching the colors obtained with a reagent containing 7-iodo-8-hydroxyquinoline sulfonic acid and ferric chloride in a hydrochloric acid solution, it is possible to determine accurately from 1 p.p.m. of fluoride in water to 10 per cent fluoride in 0.5 g. of a mineral. The following procedure is recommended by Fahey.¹¹

Reagent. Mix 90 ml. of a saturated 7-iodo-8-hydroxyquinoline sulfonic acid solution with 10 ml. of a 0.1 N solution of ferric chloride in 2 N hydrochloric acid, and add 100 ml. of water. This reagent can be kept for at least 6 months without change.

Procedure. The preliminary extraction of fluorine from rocks or minerals is carried out with few modifications according to the method of Hoffman and Lundell.¹²

By means of a pipet, transfer a 25-ml. aliquot of the unknown solution containing fluorine as sodium fluoride into a 50-ml. beaker. Into a second beaker of the same size, pipet 25 ml. of a solution having the same pH and the same concentration of sodium chloride as the unknown solution. To each beaker, add 2.00 ml. of the 7-iodo-8-hydroxyquinoline sulfonic acid-ferric chloride reagent. Then add 0.02 N sodium fluoride solution slowly from a buret (graduated to 0.05 ml.) to the beaker containing the comparison solution until the color is almost the same as that of the unknown. Then add an equal quantity of distilled water to the unknown. Fill the 2 cups of the colorimeter with the comparison and the unknown solution, respectively, and insert the plungers so that the

depth of each liquid observed is 50 mm. If the color of the unknown solution contains more yellow than that of the comparison solution, the end point has not yet been reached. Repeated additions of 0.02 N sodium fluoride are then made to the comparison solution until it is of the same color as that of the unknown in the same volume. From the volume of standard 0.02 N sodium fluoride solution, the amount of fluoride in the unknown can be calculated.

A difference in the color of the unknown and comparison solutions can be observed if the difference in the fluoride content is as little as 0.05 mg. In natural waters containing not more than 1000 p.p.m. of total solids, the sensitivity is about twice as great, thus making possible the determination of only 0.025 mg. of fluoride in 25 ml. of the solution.

Colored salts interfere with this determination, but with the exception of chromates, these may be removed by properly controlling the pH of the solution and treating with zinc oxide.^{12,13} The presence of large quantities of sodium chloride introduces considerable error, but this may be eliminated by adding the same quantity of sodium chloride to the comparison solution as is contained in the same volume of the unknown.

Urech¹⁴ has used the method of Fahey,¹¹ but recommends the following reagent:

Reagent. Heat 75 mg. of 7-iodo-8-hydroxyquinoline sulfonic acid on a water bath with 40 ml. of water to about 50° C. When the solid has all dissolved, cool, dilute to exactly 50 ml. and mix. To separate portions of this solution add one ninth as much of a solution which is 2 N in hydrochloric acid and 0.1 N in ferric chloride.

Detection of calcium, strontium, barium and zinc. 7-Iodo-8-hydroxy-quinoline sulfonic acid has been used by van Zijp¹⁵ as a sensitive microchemical reagent for calcium, barium, strontium and zinc. The reagent reacts with calcium, strontium, and barium, either in solution or as insoluble carbonates, to form orange needles. The test may be used for the detection of calcium carbonate in white lead or in zinc white, and of dolomite in magnesite.

The reagent has also been used as the basis for a delicate test for zinc salts or zinc oxide, with which it reacts to form colorless rhombic crystals.

Determination of calcium. 7-Iodo-8-hydroxyquinoline sulfonic acid reacts with calcium salts to form a bright orange-red precipitate of $3\text{Ca}(\text{C}_6\text{H}_4\text{NI-OHSO}_3)_2 \cdot 10\text{H}_2\text{O}$. This reaction can be used for the gravimetric determination of calcium in quantities as low as 5 mg. per liter. The solution from which the calcium salt is precipitated may be acid or neutral, but it must not be strongly alkaline.¹⁶

Reagents. *7-Iodo-8-hydroxyquinoline sulfonic acid:* Shake 8.8 g. of 7-iodo-8-hydroxyquinoline sulfonic acid with 200 ml. of water, and add 6.5 ml. of 4 N sodium hydroxide. Dilute to 250 ml. with water and filter.

Buffer solution: Mix 80 ml. of 30 per cent acetic acid and 10 g. of crystalline sodium acetate and dilute to 100 ml. The pH of this solution is 4.0.

Procedure. Evaporate the neutral or acid solution to be analyzed until 2.5 ml. contains not more than 2 per cent of calcium. Add 2.5 ml. of the acetate buffer and heat the mixture on a water bath. Heat 25 ml. of the 7-iodo-8-hydroxyquinoline sulfonic acid solution to boiling, and add to the calcium solution containing the buffer. Shake well. Heat on a water bath for 15 minutes, cool, and allow to stand overnight. Filter and wash the precipitate, first with the precipitating agent, then with ethyl alcohol, and finally with acetone. The precipitate is dried in air below 80° C. and weighed.

The composition of the precipitate varies very slightly with the calcium content of the solution. Magnesium, potassium and sodium do not interfere.

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2. Friedlander. 3, 964.
3. Jahresbericht der Chemischen Technologie. 625 (1894).
4. H. W. Swank and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.* 9, 406-9 (1937); *C.A.* 31, 7790 (1937).
5. A. Thiel and E. van Hengel, *Ber.* 70B, 2491-7 (1937); *C.A.* 32, 1207 (1938).
6. M. Frommes, *Z. anal. Chem.* 97, 36-49 (1934).
7. J. H. Yoe, *J. Am. Chem. Soc.* 54, 4139-43 (1932); *C.A.* 27, 39 (1933).
8. L. Urbanyi, *Mecogazdasagi Kutatasok* 15, 265-70 (1942); *C.A.* 38, 5163 (1944).
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5-METHYL-8-HYDROXYQUINOLINE

$C_{10}H_9ON$

Mol. Wt. 159.17

Beil. Ref. XXI, 110(224).



Use: Detection of copper, iron, molybdenum, palladium, titanium and tungsten.

5-Methyl-8-hydroxyquinoline is obtained as needle-like crystals from dilute alcohol. It melts at 122-124° C. It is almost insoluble in cold water, but is easily soluble in boiling water. It also dissolves in acids and solutions of alkalis with the formation of yellow colored solutions.

Preparation: Mix 10 g. of p-aminocresol hydrochloride, 24 g. of glycerol, 20 g. sulfuric acid, and 2 g. of picric acid, and heat the mixture for 3-4 hours. Dilute with water, make weakly alkaline, and strongly acidify with acetic acid, and finally distill with steam. Precipitate the reagent from the acetic acid distillate by adding ammonium hydroxide. Purify the product by recrystallizing from alcohol.¹

Reactions with metals. Color reactions are obtained when the reagent is added to a 5 per cent solution of sodium acetate in 10 per cent acetic acid containing various ions. Those ions which show the most sensitive reactions are ferric iron, palladium, copper, titanium, molybdenum, and tungsten. The sensitivities of these reactions are:

Fe ⁺³	1:1,000,000
Pd ⁺²	1:1,000,000
Cu ⁺²	1:300,000
Ti ⁺⁴	1:300,000
Mo	1:1,000,000
W	1:300,000

The test for copper, iron and palladium can be made somewhat more sensitive by adding the reagent to a 0.2 N sodium hydroxide solution which is 10 per cent saturated with sodium tartrate. Under these conditions the sensitivity of the copper and iron reactions is 1:2,500,000.²

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2. C. E. Gietz and A. Sa, *Anales asoc. quim. Argentina*, 23, 45-57 (1935); *C.A.* 30, 983 (1936).

7-NITRO-8-HYDROXYQUINOLINE-5-SULFONIC ACID

C₉H₆O₆N₂S

Mol. Wt. 270.20



Use: Detection of aluminum, barium, cadmium, calcium, cobalt, copper, lead, magnesium, nickel, potassium, strontium and zinc.

This compound is a yellowish-brown crystalline solid. It is fairly soluble in water and alcohol, but dissolves readily in acids and alkalis. It is insoluble in chloroform, ether, carbon tetrachloride and benzene. Concentrated solutions of the reagent are brown in color, but the more dilute solutions are colored intensely yellow.

Preparation: Dissolve 8-hydroxyquinoline-5-sulfonic acid in a minimum of quantity of hot concentrated hydrochloric acid and cool rapidly. Dilute the supersaturated solution with 4-5 volumes of water and add an excess of sodium nitrite. Oxidize the brown solution with a small quantity of nitric acid. On cooling, crystals of 7-nitro-8-hydroxyquinoline-5-sulfonic acid separate. Filter and purify by recrystallizing several times from water.¹

7-Nitro-8-hydroxyquinoline-5-sulfonic acid, like other 8-hydroxyquinoline derivatives, yields inner-complexes with metals (page 000).

Determination of iron. Ferric iron reacts with 7-nitro-8-hydroxyquinoline-5-sulfonic acid to form a brown compound, (C₉H₅O₆N₂S)₃Fe. The color formed in this reaction is suitable for the colorimetric determination of iron. Copper, cadmium and lead produce precipitates with the reagent and interfere with the iron determination. Acids cause a general decrease in the extinction,

and an intensely yellow solution. Alkalies depress the extinction. The optimum pH may be maintained with the aid of a biphthalate buffer.^{1,2}

Detection and determination of lead. Lead, cadmium and copper react immediately with 7-nitro-8-hydroxyquinoline-5-sulfonic acid to form insoluble compounds which may be used for the detection and determination of these metals.³ Only the lead salt, however, is sufficiently insoluble to be determined with the reagent. A solution containing 0.5 g. of lead per liter causes immediately a marked precipitation, and a solution having a lead content of 0.01 g. per liter shows a perceptible precipitation after 24 hours. The solubility of the lead salt in water is about 1 part in 100,000. A cadmium sulfate solution containing 25 g. of cadmium per liter gives an immediate precipitation, and a copper sulfate solution containing 10 g. of copper shows immediate precipitation. Comparatively, the salts of the last two metals are fairly soluble. Molar solutions of calcium chloride, barium chloride and strontium chloride yield orange-brown precipitates. Magnesium yields no similar precipitate. Molar solutions of potassium chloride, thallium nitrate and nickel nitrate yield needle-like crystals on standing for 6 hours. Sodium, chromium, manganese, aluminum, mercury, tin, zinc and ammonium salts under similar conditions form no precipitate. Ferric chloride gives a dark green color but no precipitate.

Precipitation of the lead compound takes place in neutral or acetic acid solutions. In mineral acid solutions precipitation is incomplete and the precipitate dissolves immediately on addition of sodium hydroxide.

Microchemical reactions. 7-Nitro-8-hydroxyquinoline-5-sulfonic acid reacts with a number of metallic salts to yield compounds which are useful in microchemical analysis. Among the metals which may be detected in this way are potassium, calcium, strontium, magnesium, zinc, barium, cadmium, copper, aluminum, lead, cobalt and nickel.

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2. J. Molland, *Tids. Kjemi Bergvesen Met.* **1**, 49-52 (1941).

3. J. Molland, *Tids. Kjemi Bergvesen.* **19**, 119-22 (1939); *C.A.* **34**, 1932 (1940).

5,8-QUINOLINEQUINONE-8-HYDROXY-5-QUINOLYL-5-IMIDE

$C_{18}H_{11}O_2N_3$

Mol. Wt. 301.27

$(C_9H_6NO) - N = (C_9H_5NO)$

Use: Detection and determination of copper, mercury, nickel, and silver.

This compound is a reddish-brown crystalline powder which melts at 253-254° C. It forms a 1.0 per cent solution in dioxane, but its saturated aqueous solution at 95° C. contains only 0.04 per cent of the reagent. It dissolves in mineral acids and glacial acetic acid to form red solutions, but decomposition occurs within a few hours. In dilute solutions the dye changes in color from red to blue at a pH of 6-8.

Reactions. This dye yields precipitates with at least 20 common ions. These precipitates form in acetic acid or ammoniacal solutions and are blue to bluish-

green in color. Excellent results have been obtained in determining copper, nickel and mercury when these ions are present in quantities of 1 mg. or less. The procedure recommended employs a filtration method of titration, in which the end point is attained when the filtered solution gives no test with a 0.05 per cent alcoholic solution of the reagent.

Silver salts react with the dye to give a difficultly soluble bluish-green compound. Because of this behavior, the compound has been used as an indicator for the titration of halides with silver nitrates.

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CHAPTER XIV

AZO DERIVATIVES OF 8-HYDROXYQUINOLINE

A number of interesting analytical reagents have been prepared by coupling diazotized aromatic amines with 8-hydroxyquinoline. These compounds generally give reactions with palladium, mercury, copper and molybdenum, and also with chromium, nickel, zinc, gold, silver, vanadium and bismuth.

Boyd, Degering and Shreve¹ have prepared and studied a number of these compounds.

Preparation: Diazotize the proper amine and couple with 8-hydroxyquinoline in an alkaline solution. Use distilled water in making up the alkaline 8-hydroxyquinoline solution. Purify the dyes as follows: extract the finely divided product from the first filtration with boiling water or 0.5 per cent potassium hydroxide solution and filter hot. The potassium salt separates on cooling. Convert to the dye base by stirring in an excess of acetic acid which is added to an aqueous suspension of the washed salt. Dry and crystallize from an organic solvent. Benzene is usually the most satisfactory, but other liquids may be used.²

The azo derivatives studied are:

Number	Derivative
I	5-(2-hydroxyphenylazo)-8-hydroxyquinoline
II	5-(3-hydroxyphenylazo)-8-hydroxyquinoline
III	5-(2-nitrophenylazo)-8-hydroxyquinoline
IV	5-(3-nitrophenylazo)-8-hydroxyquinoline
V	5-(4-nitrophenylazo)-8-hydroxyquinoline
VI	5-(2-chlorophenylazo)-8-hydroxyquinoline
VII	5-(3-chlorophenylazo)-8-hydroxyquinoline
VIII	5-(4-chlorophenylazo)-8-hydroxyquinoline
IX	5-(2,5-dichlorophenylazo)-8-hydroxyquinoline
X	5-(3-tolylazo)-8-hydroxyquinoline
XI	5-(2,6-dimethylphenylazo)-8-hydroxyquinoline
XII	5-(4-arsonophenylazo)-8-hydroxyquinoline
XIII	5-(3-sulfophenylazo)-8-hydroxyquinoline
XIV	5-(1-sulfo-2-naphthylazo)-8-hydroxyquinoline
XV	5-(8-hydroxy-3, 6-disulfo-1-naphthylazo)-8-hydroxyquinoline
XVI	5-(benzidine monoazo)-8-hydroxyquinoline
XVII	5,5'-(benzidine disazo)-8-hydroxyquinoline
XVIII	5-(3,3'-dimethoxybenzidine monoazo)-8-hydroxyquinoline

The compounds are used as follows:

Reagent. Prepare a saturated alcoholic solution of each of the above azo derivatives.

TABLE 51.—REACTION OF DYES WITH SOLVENTS*

Dye No.	20% Nitric Acid		20% Hydrochloric Acid		20% Aqua Regia	
	Spot Paper	Spot Plate	Spot Paper	Spot Plate	Spot Paper	Spot Plate
I	No change	RO spot	No change	RO spot	Dye bleached	Dye bleached
II	Pink stain	RO spot	RO stain	OR spot	Dye bleached	RO spot
III	ROT2 ring	ORT1 spot	ROT2	ORT1 spot	Dye bleached	RT2 spot
IV	Dye bleached	No change	Dye bleached	No change	Dye bleached	Dye bleached
V	Dye bleached	OYT1 spot	Dye bleached	OYT1 spot	Dye bleached	Dye bleached
VI	Dye bleached	No change	Dye bleached	No change	Dye bleached	Dye bleached
VII	Dye bleached ^a	No change	YOT2 spot	No change	Dye bleached	Dye bleached
VIII	Dye bleached	YOT2 spot	Dye bleached	YOT2 spot	Dye bleached	Dye bleached
IX	No change	YT2 spot	No change	YT2 spot	Dye bleached	Dye bleached
X	OT2 spot	RO spot	OT2 spot	RO spot	Dye bleached (pink ring)	Dye bleached
XI	Dye bleached ^a	OYS1 spot	Dye bleached ^a	OYS1 spot	Dye bleached	Dye bleached
XII	Dye bleached	OY spot ^b	Pink spot	OY spot ^b	Dye bleached	Dye bleached
XIII	Dye bleached	OT2 spot	Dye bleached	OT2 spot	Dye bleached	Dye bleached
XIV	VRT2 ring	RT2 spot	VRT2 ring	RT2 spot	Violet ring	Dye bleached
XV	Cinnamon spot	YO spot	Cinnamon spot	YO spot	OT1 spot	YO spot
XVI	Orange ring	OYS1 spot	Orange ring	OYS1 spot	Bright O ring ^c	Orange spot
XVII	No change	No change	No change
XVIII	No change	No change	No change

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^a Slightly. ^b Faint. ^c Then greenish fugitive ring, changing to yellow spot.

O = orange; R = red; Y = yellow; V = violet; T = tint; S = shade (3).

TABLE 52.—REACTIONS OF METALS WITH DYES *

Dye No.	Metals							Test		
	Hg ⁺⁺	Cu ⁺⁺	Pd ⁺⁺	Ni ⁺⁺	MoO ₄ ²⁻	VO ₂ ⁺ or VO ₃ ⁺	Co ⁺⁺		Fe ⁺⁺⁺	Cr ₂ O ₇ ²⁻
I	GY, r; E ORS2, s; D VR, s; A RVS2, s; A	RO, r; C ROS2, s; B VRS1, r; B RT1, s; C	GY, r; A VRT1, s; A RVS2, r; A RVS2, p; A	Neg. Neg. RT1, r, f; C Neg.	O, r; D Neg. YOS1, r; C VBS1, s; C ⁺ Neg.	GO, s, r; D YOS2, s, f; D OYS1, r; B BrGr, p; A GY, r, f; D	Neg. O, r; C Neg. Neg.	YGrS2, s, f; E YGrS2, r, f; D GY, s, f; D ⁺ GY, r, f; C	RO, r; A VRT2, s; A VR, s; A ⁺ Neg.	Paper Plate Paper Plate
II										
III										
IV										
V										
VI										
VII										
VIII										
IX										
X										
XI										
XII										
XIII										
XIV										
XV										
XVI										
XVII										
XVIII										

R = red; O = orange; Y = yellow; G = green; B' = blue; V = violet; Br = brown; Gr = gray; S = shade; T = tint (3).

r = ring; s = spot; f = fugitive; p = precipitate; + = tartrate obscures; a = hydrochloric acid enhances.

Grade rating of tests: A = excellent; B = good; C = fair; D = poor; E = very poor.

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TABLE 53.—SENSITIVITY OF REACTIONS
(mg. per ml. of solution)

Dye No.	Mercury		Palladium		MoOCl ₅ ⁻		Copper		Vanadium		Cr ₂ O ₇ ⁻	
	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop
I	3	1	0.1	0.1	+	+	0.3	+	0.3	3	0.3	0.1
II	0.3	0.1	0.1	0.1	3	3	0.3	+	0.3	0.3	0.3	0.1
III	0.3	3	+	+	+	+	+	+	0.3	+	+	1 ^a
IV	1	0.5	0.3	0.3	+	+	+	+	3	+	0.3 ^a	0.3 ^a
V	1	0.5	0.1	0.1	+	+	+	+	3	3	0.3 ^a	0.3
VI	+	3	0.1	0.3	+	+	+	+	0.3	3 ^b	0.3 ^a	0.3 ^a
VII	0.3	0.5	0.1	0.1	+	+	+	+	0.3	3 ^b	0.3	0.3 ^a
VIII	1	0.5	0.1	0.1	+	+	+	1	+	0.3	0.3-0.1 ^a	0.3 ^a
IX	+	+	+	0.3	+	+	+	+	+	+	+	0.3
X	0.5	0.5	0.1	0.1	3	+	0.3	+	0.3	3	0.3-0.1 ^a	0.3-0.1
XI	+	3	0.3	0.3	+	+	+	+	0.3	+	0.3	0.3-0.1
XII	0.5-1	3	0.1	0.3-0.1	3	3	0.3	0.3	0.3	+	0.3 ^a	0.3 ^a
XIII	3	3	0.3-0.1	0.3	1	+	0.3	+	+	+	+	0.3 ^a
XIV	3	3	0.3	0.1	+	+	0.3	0.3	0.3	+	+	0.1
XV	0.5-1	0.3	+	3-1	+	+	+	+	+	3	0.3	0.3
XVI	0.3	0.1	0.3	0.3-0.1	+	+	0.3	1	0.3	0.3-0.1	0.3	0.3

^a HCl added after test drop. ^b Fugitive.
 + = Negative test with 3 mg. ml. concentration.

Procedure. Dissolve the sample for analysis in concentrated nitric acid and evaporate to dryness. Dissolve the residue in 20 per cent nitric acid and test as follows: place a drop of the reagent on a piece of good quality filter paper and allow to stand for a moment. Then apply to the center of the spot a drop of the nitric acid solution to be tested. The test may be carried out by adding a drop of the solution to be tested to 2 drops of the reagent contained in the depression of a spot plate.

The results obtained in these studies are contained in Tables 51, 52 and 53, which are taken directly from the published work of Boyd, Degering and Shreve.

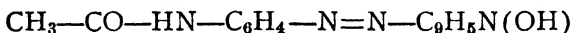
Other compounds of this type are described in the following sections.

1. T. Boyd, E. F. Degering and R. N. Shreve, *Ind. Eng. Chem., Anal. Ed.* **10**, 606 (1938).

p-ACETYLAMINOPHENYL-5-AZO-8-HYDROXYQUINOLINE



Mol. Wt. 306.28



Use: Detection of magnesium.

p-Acetylaminophenyl-5-azo-8-hydroxyquinoline is a brown-black powder. It dissolves in alcohol to form a dark brown solution. It dissolves in 20 per cent nitric acid to form a brownish-orange solution.

Preparation: Moisten 10 g. of *p*-phenylenediamine with concentrated hydrochloric acid and a little water, and triturate with 6 g. of anhydrous sodium acetate. Boil the mixture for 2 hours and cool in ice. Diazotize immediately by diluting the paste with a little water and adding about 6 ml. of concentrated hydrochloric acid and 24 ml. of a 20 per cent solution of sodium nitrite. Couple with 8-hydroxyquinoline by pouring a hot alkaline solution containing 5 g. of 8-hydroxyquinoline in small portions into the cold solution of the diazo compound. The reagent precipitates in an alkaline solution.

Detection of magnesium. An alkaline solution of *p*-acetylaminophenyl-5-azo-8-hydroxyquinoline yields a violet color with magnesium salts at a dilution of not less than 1:10,000. The following method may be used for the detection of magnesium:¹

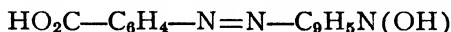
Procedure. To 2 ml. of the solution to be tested add 4 drops of a saturated alcoholic solution of the reagent, and add 1 ml. of 2 N sodium hydroxide or enough for a large excess. A violet precipitate forms if magnesium is present.

Stannous tin and metals which yield colored precipitates with alkali hydroxides must be absent. Calcium decreases the sensitivity of the test. Solid carbonates containing magnesium give a color with an alcoholic solution of the reagent.

1. G. Gutzeit, R. Monnier and R. Bachoulkova-Brun, *Compt. rend. soc. phys. hist. nat. Geneve.* **50**, 203-6 (1933); *Arch. sci. phys. nat.* **15**, July-Aug.; *C.A.* **28**, 3332 (1934).

2-CARBOXYPHENYL-5-AZO-8-HYDROXYQUINOLINE $C_{16}H_{11}O_3N_3$

Mol. Wt. 293.25

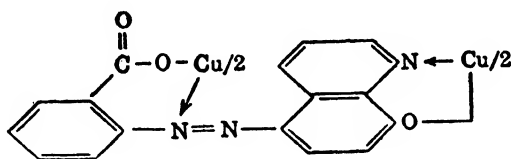
Synonym: *o*-Carbazoxine

Use: Detection of copper, mercury, molybdenum, nickel and palladium.

The compound is brown-black in color, but reflects a bluish-metallic luster. Its alcoholic solution is a deep red.

Preparation: Dissolve 5 g. of anthranilic acid in a little water with 6-8 ml. of concentrated hydrochloric acid. Diazotize with 12 ml. of cold 20 per cent sodium nitrite. Dissolve 5 g. of 8-hydroxyquinoline in 2 N sodium hydroxide and pour this solution carefully into the cold diazo solution. Acidify with hydrochloric acid and filter the precipitate. Wash quickly with the least possible quantity of water and dry on a porous plate.

Reactions. 2-Carboxyphenyl-5-azo-8-hydroxyquinoline reacts with solutions of mercury, copper, palladium, and molybdenum compounds to give color reactions or precipitates which may be used for the detection of these metals. The complexes formed by the reagent and cations may be represented by the formula for the copper compound.



The red alcoholic solution of the reagent gives a violet precipitate with mercuric ions, a purple color with cupric ions, and a characteristic violet color with bivalent palladium compounds. Silver, bismuth, trivalent arsenic, cobalt, and chromate give pale red colorations. A violet color is obtained with $(MoOCl_5)^=$ in hydrochloric acid. Cadmium, selenium, tellurium, platinum, tin, uranium, aluminum, titanium, thorium, columbium, tantalum, beryllium, yttrium, and magnesium do not react.

Spot tests may be carried out as follows:

Procedure. Evaporate to dryness the solution to be tested with concentrated nitric acid, and dissolve the residue in approximately 20 per cent nitric acid. Moisten a strip of filter paper with a drop of alcoholic solution of the reagent. Allow to dry for a moment and spot with a drop of the nitric acid solution to be tested. The following results are obtained:

Mercury	Rose-violet
Copper	Carmine-red
Nickel	Red ring
Palladium	Violet with a blue ring

To detect molybdenum, evaporate the solution to dryness with concentrated hydrochloric acid in the presence of a piece of zinc or magnesium. Dissolve the residue in dilute hydrochloric acid and proceed as above.

To carry out the reaction in a test tube, mix 0.3 ml. of the solution to be tested with 0.5 ml. of an alcoholic solution of the reagent. The results with different ions are listed above. The sensitivities of these reactions are given in Table 54.

TABLE 54.

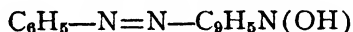
		Amount Detectable	Limiting Conc.
Mercury	Drop reaction	200 γ	1:100
	Test tube	3000 γ	
Copper	Drop reaction	200 γ	1:100
	Test tube	300 γ	1:1000
Nickel	Drop reaction	20 γ	1:1000
	Test tube	None	
Palladium	Drop reaction	1 γ	1:20,000
	Test tube	15 γ	1:20,000
$\text{MoOCl}_5^=$	Drop reaction	200 γ	1:100
	Test tube	3000 γ	1:100

1. A. Gutzeit and R. Monnier. *Helv. Chim. Acta*, **16**, 478-85, 485-6 (1933); *C.A.* **27**, 3162-3 (1933).
2. W. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934); *C.A.* **28**, 3683 (1934).

PHENYL-5-AZO-8-HYDROXYQUINOLINE

 $\text{C}_{15}\text{H}_{11}\text{ON}_3$

Mol. Wt. 289.24



Use: Detection of copper, gold, mercury, molybdenum, nickel, palladium and zinc.

The compound is a brown powder. It dissolves in alcohol to form a red solution.

Preparation: Mix 5 ml. of concentrated hydrochloric acid with 3.2 g. of aniline and dissolve with the addition of 50 g. of ice. Cool, and add 25 ml. of a 20 per cent solution of sodium nitrite. Dissolve 5 g. of 8-hydroxyquinoline in 2 N sodium hydroxide and pour this solution carefully into the diazonium salt with cooling. Allow to stand and filter. Wash, and dry on a porous plate.

Reactions. Phenyl-5-azo-8-hydroxyquinoline serves as a reagent for mercury, copper, molybdenum, gold, and zinc. With mercury, nickel, palladium, and $(\text{MoOCl}_5)^=$, violet precipitates form in nitric acid solutions, and with copper a brown precipitate is obtained. Faint tests are also given with gold and zinc. Mercury, copper, palladium, nickel, gold, and zinc may be detected either by a drop method or by a spot plate reaction.

Procedure. Dissolve a little of the material to be tested in 20 per cent nitric acid (free from chlorides), and place 1 drop of this solution on a piece of filter paper impregnated with an alcoholic solution of the reagent. Color reactions, as given above, indicate the presence of various cations.

Mercury may be eliminated by heating the material to be tested to red heat before dissolving in nitric acid. Tartrate ions mask copper, palladium, and nickel; and chlorides mask the mercury and palladium reactions.

No reaction is obtained with cadmium, selenium, tellurium, platinum, tin, uranium, aluminum, titanium, thorium, columbium, tantalum, beryllium, yttrium, and magnesium.

The sensitivities of the above reactions are given in Table 55.

TABLE 55.

		Amount Detectable	Conc. Limit
Mercury	Drop reaction	5 γ	1:4000
	Test tube	100 γ	1:200
Copper	Drop reaction	20 γ	1:1000
	Test tube	3000 γ	1:100
Palladium	Drop reaction	5 γ	1:4000
	Test tube	3000 γ	1:100
Nickel	Drop reaction	20 γ	1:1000
	Test tube	3000 γ	1:100
Molybdenum		Not sensitive	

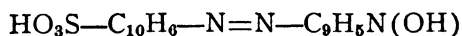
1. A. Gutzeit and R. Monnier, *Helv. Chim. Acta*, **16**, 478-85, 485-6 (1933); *C.A.* **27**, 3162-3 (1933).
2. W. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934).
3. C. F. Miller, *Chemist-Analyst*, **25**, 86-7 (1936).

5-(4-SULFO-1-NAPHTHYLAZO)-8-HYDROXYQUINOLINE

$C_{19}H_{13}O_4N_3S$

Mol. Wt. 379.35

Synonym: Naphthazoxine



Use: Detection of chromium, mercury and palladium.

This reagent is a brown-red powder. It dissolves in ethyl alcohol to form an orange solution. It also dissolves in dilute acids to form yellow solutions, and in concentrated acids to form a violet-black color. These solutions become red when made alkaline.

Preparation: Dissolve 6 g. of sodium naphthionate in a solution of 3-5 g. of sodium carbonate in 35 ml. of water. Cool in ice and acidify with 9 ml. of 20 per cent hydrochloric acid. Diazotize rapidly (3-5 minutes) with 12 ml. of a 20 per cent solution of sodium nitrite. Dissolve 5 g. of 8-hydroxyquinoline in sodium hydroxide and pour this solution into the diazo mixture. Coupling takes place immediately and the dye is precipitated. If the solution is not alkaline add

a little sodium carbonate. Stir for a time and allow the mixture to stand for 1 hour. Filter and wash with ice water. Dry on a porous plate.

Detection of chromium, mercury and palladium. Naphthazoxine reacts with solutions of palladous nitrate in dilute nitric acid to give an orange-brown coloration and then a red precipitate. The reagent also gives a pink coloration with solutions of mercury salts, and a pure green color with concentrated solutions of chromates. The formula for the complexes formed with this reagent is similar to that of the metallic complexes of 8-hydroxyquinoline. The reaction with palladium may be used as a sensitive test for that metal, but the chromate and mercury reactions are not sufficiently sensitive to be of great analytical value.

Palladium may be detected by a spot test which is carried out as follows:

Reagent. Prepare a cold saturated solution of the reagent in alcohol.

Procedure. Evaporate the solution to be tested to dryness with concentrated nitric acid and dissolve the residue in 20 per cent nitric acid. Moisten a strip of filter paper with a drop of the reagent and let stand for a moment. Then treat with a drop of the nitric acid solution to be tested. A spot or orange ring indicates the presence of palladium. The spot becomes more perceptible by moistening with a drop of water.

The test may be performed by mixing 0.3 ml. of the solution to be tested with 0.5 ml. of the reagent. A color change to orange, followed by the formation of a red precipitate (if the concentration of palladium is great enough) indicates palladium.

By means of the spot test, 2.0 γ of Pd may be detected, while with the latter method 30 γ may be detected. When the ratio of mercury:palladium is 50:1, 20 γ of palladium may be detected. The reaction is less sensitive in the presence of chlorides.

Mercuric ions may give a faint rose ring or color. On a spot plate, 3 mg. of mercury gives a test. Chromate gives a green spot with 2 mg. (1:100), or on a plate 3 mg. (1:1000) gives a test. Interference by chromate may be eliminated by reduction with zinc.

1. G. Gutzeit and R. Monnier, *Helv. Chim. Acta*, **16**, 233-8 (1933); *C.A.* **27**, 2649 (1933).
2. W. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934); *C.A.* **28**, 3683 (1934).

5-(p-SULFOPHENYLAZO)-8-HYDROXYQUINOLINE

Synonym: Sulfenazoxine

$C_{15}H_{11}O_4N_3S$

Mol. Wt. 329.30



Use: Detection of chromium, copper, mercury, molybdenum, nickel, palladium, silver and vanadium.

This compound is obtained as a brown powder. It dissolves in ethyl alcohol to form a yellow solution.

Preparation: Dissolve 12 g. of sulfanilic acid in 70 ml. of water containing 4 g. of sodium carbonate and add 20 ml. of hydrochloric acid ($d = 1.19$). Cool with ice and into this mixture pour slowly (over period of 10 minutes) with stirring, 25 ml. of a 20 per cent solution of sodium nitrite. Dissolve 10 g. of 8-hydroxyquinoline in dilute hydrochloric acid. Neutralize with sodium carbonate and dissolve the precipitate thus formed with a little dilute acetic acid. Pour this solution into the diazonium salt, which is cooled in ice. Shake and allow to stand for 1 hour, and neutralize with sodium carbonate. Allow to stand overnight and filter. Wash with cold water and dry.

Reactions. Mercury, copper, palladium, nickel, pentavalent molybdenum, vanadium, silver, and chromates may be detected, either by means of spot tests or by drop reactions.^{1,2}

Reagent. Prepare a saturated solution of the reagent in alcohol.

Procedure. Evaporate the solution to be tested to dryness with concentrated nitric acid, and dissolve the residue with 20 per cent nitric acid. Moisten filter paper with the alcoholic solution of the reagent and let dry a few moments. Treat with the nitric acid solution to be tested. Compare the spot with a reference drop of 20 per cent nitric acid. A red-violet spot forms with mercury and copper, while palladium gives a red spot and nickel a red ring.

With a spot plate use 0.3 ml. of the solution to be tested and 0.5 ml. of the reagent.

With mercuric nitrate, a bright red precipitate is formed, but this is destroyed in the presence of a chloride. Red precipitates are also obtained with copper and palladous ions, and brown precipitates with pentavalent molybdenum, vanadic compounds, and chromates.

The sensitivities of the above reactions are given in Table 56.

TABLE 56.—SENSITIVITY

Ion	Spot Test	Spot Plate
Hg ⁺⁺	50 γ (1:4000)	75 γ (1:5000)
Pd ⁺⁺	200 γ (1:100)	30 γ (1:10,000)
Cu ⁺⁺	200 γ (1:1000)	300 γ (1:1000)
Ni ⁺⁺	20 γ (1:10,000)	0.03 g. (1:10)
Mo ⁺⁵	300 γ (1:1000)	Not sens.
V ⁺⁵	Not sens.	300 γ (1:1000)
CrO ₄ ⁻	Not sens.	300 γ (1:1000)

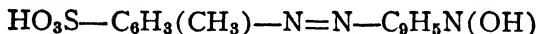
1. G. Gutzeit and R. Monnier, *Helv. chim. Acta*, **16**, 233-8 (1933); *C.A.* **27**, 2649 (1933).
2. W. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934); *C.A.* **28**, 3683 (1934).

p-(4)-SULFO-o-TOLYL-5-AZO-8-HYDROXYQUINOLINE

Synonym: Sulfotolazoxine

 $C_{16}H_{13}O_4N_3S$

Mol. Wt. 343.32

**Use:** Detection of mercury and palladium.

The compound is brown-orange in color. It dissolves in methyl alcohol and ethyl alcohol to form orange solutions.

Preparation: (a) *p-Sulfo-o-toluidine*: Mix 20 g. o-toluidine and 11 g. concentrated sulfuric acid and heat to 180° C. When the mixture becomes fluid, add, while still hot, 2 g. of oxalic acid. Heat for some time, and pour onto an iron plate which is maintained at a temperature of 180° in an oven for 7 hours. Cool and pulverize, and boil with 1200 ml. of water. Make alkaline with calcium hydroxide, and add 12 g. of 30 per cent hydrochloric acid. Cool in ice, and after 12 hours filter off the sulfonic acid. Evaporate the filtrate and combine the precipitates. Wash the solid with benzene and allow to dry.

(b) *Sulfotolazoxine*: Dissolve 7 g. of dried sulfonic acid in 35 ml. of a 10 per cent solution of sodium carbonate. Cool in ice and add 9 ml. of 20 per cent hydrochloric acid, and then pour in slowly 12 ml. of 20 per cent sodium nitrite solution. Dissolve 5 g. of 8-hydroxyquinoline in 2 N sodium hydroxide and pour slowly into the solution of the diazonium salt. If the mixture is still acid, make alkaline. Shake and let stand. Filter and wash with tepid water.

Detection of mercury and palladium. Mercuric and palladous ions may be detected by the red color which is formed when they react in a nitric acid solution with an alcoholic solution of the reagent. Palladium yields only a faint red color. The above metals may be detected by means of spot tests or drop reactions. These are carried out as follows:^{1,2}

Reagent. Dissolve the reagent in boiling ethyl alcohol (to avoid chlorides) and evaporate to dryness. Dissolve the residue in methyl alcohol, and use this solution as the reagent.

Procedure. Evaporate the solution to be tested to dryness with concentrated nitric acid, and dissolve the residue in 20 per cent nitric acid. Moisten a strip of filter paper with the methyl alcohol solution of the reagent (freshly prepared). Let dry for a moment and spot with a drop of the nitric acid solution to be tested. Compare with a reference spot formed with 20 per cent nitric acid. A rose color indicates mercury.

With a drop plate reaction, use 0.3 ml. of solution to be tested with 0.5 ml. of reagent. A vermilion color is obtained with mercury.

Palladium reacts similarly, although the reaction is very faint. Cadmium, selenium, tellurium, platinum, tin, uranium, aluminum, titanium, thorium, tan-

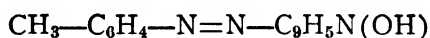
talum, beryllium, yttrium, and magnesium do not react, but the presence of chlorides hinders the reaction. With the use of a spot technique, 100 γ of mercury may be detected at a dilution of 1:100, while with the use of a spot plate 1500 γ may be detected at a dilution of 1:200.

1. G. Gutzeit and R. Monnier, *Helv. Chim. Acta.* **16**, 478-85, 485-6 (1933); *C.A.* **27**, 3162-3 (1933).
2. W. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934); *C.A.* **28**, 3683 (1934).

p-TOLYL-5-AZO-8-HYDROXYQUINOLINE Synonym: p-Tolazoxine

$C_{16}H_{13}ON_3$

Mol. Wt. 263.26



Use: Detection of bismuth, copper, mercury, molybdenum, palladium and silver.

This compound is violet-brown in color, but dissolves in alcohol with the formation of a red-orange solution.

Preparation: Pour 10 ml. of concentrated hydrochloric acid onto 4 g. of *p*-toluidine and add 4 ml. of water. Boil to dissolve the product and cool in ice, and then diazotize with 12 ml. of 20 per cent sodium nitrite. Dissolve 5 g. of 8-hydroxyquinoline in 2 N sodium hydroxide and pour this solution into the cold diazonium salt. Filter, wash, and dry on a porous tile.

Reactions. *p*-Tolyl-5-azo-8-hydroxyquinoline gives a violet-red precipitate with mercury, a violet precipitate with copper, and a brownish-violet precipitate with palladous salts. In nitric acid solutions, faint olive-green reactions are obtained with silver and bismuth. Ruthenium, osmium, iridium, arsenic, nickel, and chromate give brown precipitates. Cadmium, selenium, tellurium, platinum, tin, uranium, aluminum, titanium, thorium, columbium, tantalum, beryllium, yttrium and magnesium do not react.^{1,2}

Detection of molybdenum. In the presence of hydrochloric acid, which masks reactions with mercury, copper, palladium, silver, and bismuth, a violet precipitate is obtained with $(MoOCl_5)^=$. This reaction may therefore be used satisfactorily as a test for molybdenum when less than 5 per cent of copper is present.

Procedure. First form $MoOCl_5^=$ by reducing a hydrochloric acid solution of an alkali molybdate by evaporating the solution to be tested on a water bath with hydrochloric acid and zinc or magnesium. Take up the residue with 20 per cent hydrochloric acid. Impregnate filter paper with an alcoholic solution of the reagent, and touch with the acidified solution to be tested. A violet spot or ring indicates molybdenum.

The sensitivities of the *p*-tolazoxine reactions are given in Table 57.

TABLE 57.

Ion		Amount Detectable	Limiting Conc.
Hg ⁺⁺	Drop reaction	20 γ	1:1000
	Test tube	300 γ	1:1000
Cu ⁺⁺	Drop reaction	2000 γ	1:20
	Test tube	3000 γ	1:100
Pd ⁺⁺	Drop reaction	20 γ	1:1000
	Test tube	300 γ	1:1000
MoOCl ₅ ⁼	Drop reaction	20 γ	1:1000
	Test tube	3000 γ	1:100

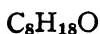
1. A. Gutzeit and R. Monnier, *Helv. Chim. Acta*, **16**, 478-85, 485-6 (1933) ; *C.A.* **27**, 3162-3 (1933).
2. W. Fresenius, *Z. anal. Chem.* **96**, 433-6 (1934) ; *C.A.* **28**, 3683 (1934).

CHAPTER XV

ETHERS

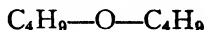
The ethers are very inactive compounds, but have many useful applications as solvents and wash liquids in analytical procedures.

DIBUTYL ETHER



Mol. Wt. 130.22

Beil. Ref. I, 369.



Use: Determination of bismuth.

Dibutyl ether is a colorless liquid of mild, ether-like odor. It boils at 142° C. Its sp. gr. is 0.769. The ether is practically insoluble in water and can be used in place of ethyl ether for extractions. Because of its higher boiling point, and the fact that it may now be obtained commercially, this ether may be expected to replace ethyl ether in many analytical procedures.

Preparation: Mix 600 g. of butyl alcohol and 200 g. of concentrated sulfuric acid and heat until the temperature reaches 134° C. Distill the mixture in a current of steam. Separate the ether in the distillate from water, and wash with a solution of an alkali. Fractionally distill, and retain the fraction boiling at 142.5-144° C.¹

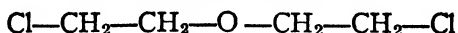
Determination of bismuth. A 30 per cent solution of acetone in dibutyl ether has been proposed as a wash liquid for the precipitation of bismuth as the quinaldine salt of iodobismuthous acid.² The ether has also been used as a wash liquid for the caffeine salt of iodobismuthous acid in a method proposed for the determination of bismuth by Beale and Chandlee (section on caffeine).³

1. I. N. Hultman, A. W. Davis, and H. T. Clarke, *J. Am. Chem. Soc.* **43**, 368 (1921).
2. J. R. Hayes and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.* **11**, 531-2 (1939); *C.A.* **33**, 9186 (1939).
3. R. S. Beale and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.* **14**, 43-4 (1942); *C.A.* **36**, 987 (1942).

β,β -DICHLORODIETHYL ETHER



Mol. Wt. 143.02



Use: Determination of iron.

This reagent is a colorless, clear liquid, which possesses a pungent odor. Its sp. gr. is 1.22, and it boils at 178° C. It is insoluble in water, but is soluble in most organic solvents.

Methods of preparation have been studied by Schoeller,¹ and by Nekrassow and Komissarow.²

Determination of iron. The mutual solubility of β,β -dichlorodiethyl ether and aqueous solutions of hydrochloric acid is so small that extractions are practicable with quite concentrated solutions of acids. Distribution data of ferric chloride between hydrochloric acid solutions and the ether indicate that this compound can be used for the quantitative extraction of ferric chloride from solutions having hydrochloric acid concentrations greater than 7 N.³

1. W. Schoeller, *Chem. Zentr.* I, 801 (1927).
2. W. Nekrassow and J. Komissarow, *J. pr. Chem.* [2] 123, 160-80 (1929).
3. J. Axelrod and E. H. Swift, *J. Am. Chem. Soc.* 62, 33-6 (1940); *C.A.* 34, 1220 (1940).

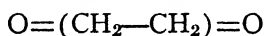
DIOXANE

Synonym: Diethylene oxide, 1,4-dioxane



Mol. Wt. 88.10

Beil. Ref. XIX, 3.



Use: Separation of lithium from potassium and sodium.

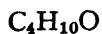
Dioxane is a colorless liquid. It boils at 101.4° C. and melts at 11.8° C. Its sp. gr. is 1.0336. It is miscible with water and most organic solvents.

Separation of lithium from potassium and sodium. Dioxane which has been dehydrated by heating with sodium dissolves lithium salts but not the corresponding salts of sodium and potassium. Lithium chloride and lithium nitrate are more soluble than lithium sulfate. Lithium chloride may be extracted completely in the pure state from a mixture of the chlorides of lithium, potassium, and sodium.^{1,2}

1. A. Sinka, *Z. anal. Chem.* 80, 430-5 (1930); *C.A.* 24, 4235 (1930).
2. C. Cimermann and C. J. Rzymowska, *Mikrochemie.* 20, 129-43 (1936); *C.A.* 30, 5144 (1936).

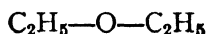
ETHYL ETHER

Synonym: Ether



Mol. Wt. 74.12

Beil. Ref. I, 314.



Use: Detection of ammonia, boron, cadmium, chromium, cobalt, copper, mercury, nickel, osmium, platinum, ruthenium, zinc.

Determination of aluminum, ammonia, barium, bismuth, boron, calcium, cerium, cobalt, gallium, gold, iron, lithium, mercury, molybdenum, nickel, osmium, phosphorus, potassium, rhenium, selenium, silver, sodium, strontium, thallium, thorium, uranium, and zinc.

Ether is a colorless, volatile liquid boiling at 34.5° C. It has a sp. gr. of 0.7135 and a refractive index of 1.35424 at 17.1° C. Its solubility in water at 20° C. is 7.42 per cent by weight, and at 30° C. it is 5.64 per cent. It is miscible in all proportions with ethyl alcohol, chloroform and benzene. It is very inflammable, and air mixtures containing 75-200 p.p.m. explode violently.

Extraction of metals. Ether may be used in a number of important separations which are based upon the extraction of metallic salts, usually the chlorides, from dilute hydrochloric acid solutions. The chlorides of iron, gold, thallium, gallium and molybdenum can be extracted to the extent of about 90 per cent, whereas with germanium, arsenic and antimony the extraction is from 50-90 per cent complete. Iridium, phosphorus, tin and tellurium are also extracted but to the extent of less than 50 per cent. The concentration of hydrochloric acid greatly influences the amount of metallic chloride that is extracted with ether.

Mylius and Huttner^{1,2} have studied the extraction of various metallic chlorides with ether in hydrochloric acid solutions of different concentrations, and their results are given in Table 58. This table gives the per cent of total metal present that is extracted by 100 ml. of ether on shaking with a solution containing 1 g. of the metal in a volume of 100 ml.

Since chlorides are often extracted by ether from solutions which are 5-6 N in hydrochloric acid, Swift³ has studied the behavior of various chlorides on shaking a 6 N hydrochloric acid solution with ether. These results are given in Table 59.

TABLE 58.—EXTRACTION OF METALLIC CHLORIDES WITH ETHER

Chloride	Medium					
	Water	1% HCl	5% HCl	10% HCl	15% HCl	20% HCl
HgCl ₂	69.4	13	0.4	0.2
HAuCl ₄	40.3	85	98	98.2	95
FeCl ₃	Trace	0.1	8	92	99
SbCl ₃	0.3	8	22	13	6
SbCl ₅	Trace	2.5	6	22	81
SnCl ₄	0.8	10.	23	28	17
AsCl ₃	0.2	0.7	7.3	37	68
TeCl ₄	Trace	0.2	3.0	12	34
CuCl ₂	Trace	0.05	0.05
ZnCl ₂	Trace	0.03	0.2
NiCl ₂	Trace	0.01	Trace
PbCl ₂
AgCl
PtCl ₄	Trace	Trace	0.01	Trace
PdCl ₂	0.02	Trace	0.01
H ₂ IrCl ₆	Trace	Trace	0.02	5

TABLE 59.—EXTRACTION OF ELEMENTS FROM 6N HYDROCHLORIC ACID

Metal	% Extracted	Metal	% Extracted
Aluminum	0	Molybdenum (MoO_3)	80-90
Antimony (SbCl_3)	6	Nickel	0
Antimony (SbCl_5)	81	Osmium	0
Arsenic (AsCl_3)	68	Palladium	0
Arsenic (AsCl_5)	2-4	Platinum	Trace
Beryllium	0	Rare earths	0
Bismuth	0	Rhodium	0
Cadmium	0	Selenium	Trace
Chromium	0	Silver	0
Cobalt	0	Tellurium	34
Copper	Trace	Thorium	0
Gallium	97	Thallium (TlCl_3)	90-95
Germanium	40-60	Tin (SnCl_4)	17
Gold	95	Tin (SnCl_2)	15-30
Indium	Trace	Titanium	0
Iridium	5	Tungsten	0
Iron (FeCl_3)	99	Uranium	0
Iron (FeCl_2)	0	Vanadium (V_2O_5)	Trace
Lead	0	Zinc	Trace
Manganese	0	Zirconium	0
Mercury	Trace		

Separation of iron. Perhaps the most widely used and extensively studied of the ether separations is that proposed by Rothe⁴⁻⁷ and used by others⁸⁻¹⁰ for the extraction of ferric chloride. This principle is often used for the removal of iron as a preliminary to the determination of nickel, manganese, cobalt, copper, aluminum, titanium, vanadium and chromium in samples of iron and steel. This separation is illustrated by the following procedure for the determination of manganese in iron and steel.⁷

Reagents. *Ether-hydrochloric acid solution:* Add ether in small portions to concentrated hydrochloric acid ($d = 1.19$) until a layer of ether remains on the surface of the acid solution after shaking. One volume of the concentrated acid dissolves about 1.5 volumes of ether.

Dilute ether-hydrochloric acid solution: Add small portions of ether to 6 N hydrochloric acid as described above. One volume of 6 N acid dissolves about 0.5 volume of ether.

Procedure. Dissolve about 10 g. of sample, containing less than 1 per cent of manganese, with 7.5 N nitric acid, using 15 ml. of the acid for each gram of the metal. When the reaction has subsided, heat the mixture on a wire gauze until solution is complete and brown fumes are no longer evolved. Evaporate to dryness and gently bake the residue. Dissolve in 50 ml. of 6 N hydrochloric acid and heat until all ferric oxide and basic salt has dissolved. Dilute to 150 ml. and filter. Wash the residue of silica and add the washings to the filtrate.

Evaporate the filtrate to a thick syrupy liquid, avoiding the separation of crystals. Transfer this solution to a separatory funnel and wash the dish with 6N hydrochloric acid until no yellow coloration appears when the acid is added to the dish. Add the acid in 3-ml. portions. Ten to 15 ml. of acid should be sufficient. Shake the solution in the funnel and cool with running water. For each gram of metal used add 6 ml. of the concentrated hydrochloric acid that has been saturated with ether. Mix, and nearly fill the funnel with pure ether. Shake well and cool under running water. Allow the liquids to separate and draw off the lower layer into a second separatory funnel. Allow the original funnel to stand for a short time until a little acid separates below the ether. Carefully transfer this to the second separatory funnel without allowing any of the ether layer to pass through the stop cock. Add 3 ml. of the dilute ether-hydrochloric acid mixture and again drain off the lower layer into the second separatory funnel. Now add 10 ml. of the dilute-ether acid mixture to the first separatory funnel and nearly fill the second funnel with ether. Shake well and draw off the lower layer in the second funnel into a porcelain dish. Drain off the lower layer of the first funnel into the second funnel and rinse with a little dilute-ether acid mixture. Withdraw the lower layer of the first funnel into the second and the lower layer of the second into the dish. After repeating this washing 3 or 4 times, the manganese, together with nickel, cobalt, aluminum, chromium, sulfuric acid and phosphoric acid are in the dish. Remove the ether by evaporation on a water-bath and finally evaporate to dryness. Dissolve in 5 ml. of 6N hydrochloric acid and use this solution for the determination of the metals which it contains.

According to Wada,^{11,12,13} indium chloride is not extracted under the same conditions as iron, but Ato¹⁴ claims small quantities of indium may be present in the ether layer. This, however, may be removed by a single extraction with 4-7 N hydrochloric acid. Wysor^{15,16} claims that about 35 per cent of the phosphorus remains with the iron in the ether layer in the presence of 3 g. of iron.

Deiss and Leysaht^{17,18} have applied the Rothe method to the separation of iron and vanadium. This method is said to give low results, since some pentavalent vanadium passes into the ether solution. This is indicated by a yellow color. By reducing the vanadium to V_2O_4 with sulfur dioxide, no vanadium passes into the ether layer until after standing for several days. Since the time required for the analysis is very short the error due to the ether extraction of vanadium is negligible. Ordinary ether contains peroxides, which change the pure blue hydrochloric acid solution of V_2O_4 to blue-green or green due to the formation of pervanadic acid and this compound is insoluble in ether. Since sulfur dioxide also reduces ferric iron to the ferrous state, and since the latter is insoluble in ether, most of the vanadium should be removed by the usual method. The ether solution of ferric chloride, which contains the remainder of the vanadium, should then be extracted with hydrochloric acid saturated with ether and containing hydrogen peroxide.

Kern¹⁹ has used ether for the extraction of iron in the analysis of uranium. Shkotova²⁰ recommends extracting a concentrated hydrochloric acid solution of a sample of ferromolybdenum 2 or 3 times with ether to remove iron and

molybdenum prior to determining tin by precipitating as the sulfide. Various investigators^{21,22,23} have used ether for extracting iron as a preliminary to the determination of nickel and cobalt in steel.

Ferric thiocyanate may be extracted with a mixture of amyl alcohol and ether.⁹¹ Rode²⁴ has used ether with amyl alcohol for the removal of iron as iron thiocyanate before determining aluminum with 8-hydroxyquinoline. Traces of lead may also be separated quantitatively from considerable quantities of iron by removing the latter with ether.²⁵ Noyes and co-workers²⁶ have used ether for separating iron and thallium from zirconium and titanium in a systematic scheme of analysis. Titanium, zirconium and also uranium are not extracted. Phosphoric acid does not interfere. Chandelle²⁷ has used ether to eliminate interference due to iron in the analysis of zirconium with methylarsonic acid.

Bismuth reacts with potassium thiocyanate to give an intense yellow color, due probably to the formation of $K_3[Bi(SCN)_6]$. This reaction is used for the detection and determination of bismuth. The solution to be analyzed is acidified with fairly concentrated hydrochloric acid, diluted, and treated with a large excess of potassium thiocyanate. The color is extracted with ether only in highly concentrated solutions, and this makes possible the separation of iron and bismuth, since ferric thiocyanate is soluble in ether. Molybdenum also forms a yellow thiocyanate which is removed by ether extraction.²⁸

Steinhaus²⁹ has used ether to extract ferric thiocyanate in the colorimetric determination of iron. Iron may be extracted from aqueous solutions with ether after treating with cupferron.^{92,93} A 1:1 mixture of ether and benzene⁹⁴ may be used.

Separation of gallium. Gallium may be separated from other elements since it is extracted almost completely by ether from 5-6 N hydrochloric acid solutions.³ Various other elements (see table page 360) are also extracted with ether under these conditions but a number of useful separations may be made.

According to Ato,⁸⁰ gallium may be separated from beryllium, titanium, zirconium and thorium by a procedure based on the following steps:

Procedure. Shake 25 ml. of a chloride solution in approximately 5-6 N hydrochloric acid ($d = 1.093$) and containing 0.02-0.26 g. of $GaCl_3$ with 3 separate portions of ether. Wash the ether after each treatment with 5 ml. of fresh acid. The greater part of the gallium passes into the ether solution. Recover the gallium remaining in the aqueous solution by evaporating to dryness, dissolving in water, boiling with ammonium acetate and ammonium hydroxide, filtering and uniting the filtrate with the gallium chloride which was extracted with ether. Remove the ether and precipitate gallium in a solution made barely acid with acetic acid by the addition of 2 g. of sodium camphorate. Filter the precipitate, ignite and weigh as Ga_2O_3 .

Scherrer⁸¹ has used a similar method for the determination of gallium in aluminum. Gallium is extracted as the chloride from a solution that is 6 N in hydrochloric acid. The total volume of the solution is 400 ml., and three

150-ml. portions of ether serve to remove all gallium. The final determination is made by precipitating the metal with cupferron.

Ether has also been used to extract gallium before applying confirmatory tests with alizarin or with a ferrocyanide and manganous salt.^{32,33}

Extraction of thallium. Thallium may be separated from various other metals by extracting the trichloride or the tribromide with ether from dilute hydrochloric or hydrobromic acid solutions, respectively. The most favorable concentration of hydrogen bromide is 1.0 N. Thallium bromide, $TlBr_3$, may be separated from all other metal salts except gold by shaking the hydrobromic acid solution with ether. After two extractions only 0.2 per cent of the total thallium remains in the aqueous layer. Gold is also extracted under the same conditions, but in the presence of potassium cyanide, and after the removal of ether, the tribromide can be reduced to insoluble thalious bromide by treating with hydroxylamine hydrochloride, which does not reduce gold.^{34,35,36}

Separation of thorium and uranium. Misciattelli^{37,38} has studied the solubility of uranyl and thorium nitrates in ether and reports that thorium nitrate, $Th(NO_3)_4$, is undissolved only in ether solutions saturated with a uranyl salt at temperatures above 20° C.

Extractions in quantitative and qualitative analysis. Ether is very frequently used to extract the colored products of many reactions which are used for the detection and determination of various substances. In this way the sensitivity of many reactions is greatly increased. By the use of ether as an immiscible liquid with aqueous reaction mixtures, reaction products are frequently collected at the interface, thereby increasing the sensitivity of the test. A few illustrations typical of these uses are given in the following sections:

(a) Determination of molybdenum. A blood-red solution of molybdenum thiocyanate is formed when a thiocyanate is added to a solution of reduced molybdenum. Ether is used as a solvent for extracting the molybdenum thiocyanate and the colored solution is matched against standards in a colorimeter.¹³ Extraction with ether increases the stability of the colored products and also increases the sensitivity of the reaction.³⁹ A 2:1 ether-petroleum ether mixture that has been shaken with thiocyanate and stannous chloride is also recommended.

Molybdenum may be determined by the red color formed in the reaction with potassium xanthogenate. The red color is extracted with a mixture of ether and petroleum ether or with chloroform prior to the comparison.^{88,89,90} For the details of this method, see section on potassium xanthogenate.

When a molybdate solution is acidified with hydrochloric acid and treated with an excess of sodium thiosulfate, sulfur is precipitated and molybdenum is reduced to a colored compound which can be extracted with ether or ethylacetate. The color of the ether solution is suitable for colorimetric comparison, using a series of standards method. The color varies from lilac to rose to red-brown depending on concentration. The reaction is more sensitive than those with stannous chloride, hydrogen peroxide or potassium xanthate. The color is not affected by tartaric, citric or oxalic acids, ammonium salts, chromates and

chlorates. Copper and iron may interfere, and alkalis destroy the color. The following method may be used for the determination of molybdenum in steel.

Procedure. (a) Dissolve 1-2 g. of steel in aqua regia and evaporate to dryness. Dissolve the residue in 10 ml. of concentrated hydrochloric acid and dilute with water to 30-40 ml. Filter and dilute to 100 ml. To a 10-ml. aliquot add 2 ml. of concentrated hydrochloric acid and extract with 8 ml. of a mixture of 80 per cent ethyl acetate and 20 per cent ether. Shake the organic extract with an equal volume of 30 per cent sodium thiosulfate solution. Separate the layers and again extract with a second sodium thiosulfate solution. Filter the solvent layer and compare with a series of standards prepared from steels of known molybdenum content.

(b) **Detection of platinum.** The addition of stannous chloride to a platinum solution produces a red color which can be extracted with ether.⁴⁰

(c) **Detection and determination of zinc.** Zinc may be detected by the blue zone which forms at the interface between ether and water when an ether solution of resorcinol is added to an ammoniacal solution of zinc^{41,42} (page 177).

Vanossi⁴³ recommends separating zinc as zinc thiocyanate with ether in the dithizone method for determining zinc.

(d) **Detection of copper.** A blue color forms when an excess of ammonia and 1-2 drops of phenol are added to 5 ml. of a solution containing a trace of copper. On shaking with ether the blue color collects at the zone of contact of the two liquids.⁴⁴

(e) **Detection of ruthenium and detection and determination of osmium.** When a ruthenium solution is heated with thiocarbanilide, a blue-green color appears, which can be extracted with ether. This reaction is sensitive to 0.0003 mg. ruthenium per ml. A solution of osmium in concentrated hydrochloric acid gives a red color when heated with thiocarbanilide, and the sensitivity of this reaction is increased by shaking with ether. An olive-green color is formed when osmium and hydrochloric acid are treated with potassium thiocarbonate and extracted with ether.⁴⁵ This reaction will detect 0.02 mg. of the osmium in 100 ml. of solution. Osmium may also be detected and determined by a color reaction which is obtained with potassium thiocyanate and ether.⁴⁶

(f) **Detection and determination of nickel.** Ether may be used to extract nickel dimethylglyoxime for the colorimetric determination of nickel.⁴⁷ Alvarez⁴⁸ has used ether saturated with hydrogen chloride as a reagent for nickel. Nickel is precipitated as the anhydrous chloride. The sensitivity of this reaction is 1 mg. of nickel in the presence of 1 g. of cobalt.

(g) **Detection and determination of cobalt.** Ether may be used to extract the color formed in the well-known Vogel test for cobalt using potassium thiocyanate.^{49,50,51}

The following method may be used for the colorimetric determination of cobalt in the presence of nickel.⁵²

Procedure. Dissolve 1 g. of the substance to be tested in 25 ml. of water and add 5 ml. of 1:1 ammonium thiocyanate and 10 ml. of 2:5 mixture of isoamyl alcohol and ether and 5 ml. of 1:2 ammonium acetate. Shake, add 3 drops of 10 per cent tartaric acid, again shake and compare the color of the alcohol-ether layer with that of standards.

(h) Detection and determination of boron. Boric acid is volatile with ether, although almost entirely insoluble in anhydrous ether. Boric acid may therefore be separated from other materials by acidifying a solution of the borate and boiling with ether in a special extraction apparatus.^{53,54}

The colored product in the reaction between boric acid and turmeric is soluble in ether and may be extracted to increase the sensitivity of the test.⁵⁵

(i) Determination of phosphorus. Phosphorus may be determined colorimetrically in steel and cast iron by extracting the phosphomolybdate complex with ether. The phosphomolybdate is reduced with stannous chloride.^{56,57}

(j) Detection and determination of mercury. Mercuric salts react with cryogenin to form a pink color and then a violet precipitate. On shaking the mixture with ether the precipitate collects at the interface and is more easily observed.⁵⁸

Mercury may be determined by a method based on the solubility of mercuric iodide in ether and its insolubility in water. Phosphoric acid or citric acid is added to reduce the solvent effect of potassium iodide.⁵⁹

Procedure. To 25 ml. of a solution of a mercuric salt, add dropwise a 5 per cent solution of potassium iodide to precipitate mercuric iodide. Avoid an excess of potassium iodide. Add a few drops of phosphoric acid ($d = 1.75$) and 50 ml. of ether. Shake vigorously and allow the liquid layers to separate. Draw off the aqueous layer and repeat the extraction with 50 ml. of ether. Repeat three times and wash the combined ether extracts three times with small quantities of distilled water. Evaporate the ether, dry the residue and weigh as mercuric iodide.

(k) Detection of chromium. Chromium is frequently detected by converting to perchromic acid with hydrogen peroxide. The perchromic acid is extracted with ether in which it dissolves with an intense blue coloration.^{60,61,62}

(l) Detection and determination of ammonia. When thymol and a hypobromite are added to a dilute solution of ammonia, a blue color is formed which dissolves in ether to give a deep red solution.^{63,64,65}

Meurice⁶⁶ has developed a method for the titrimetric determination of ammonia which employs ether. This is carried out as follows:

Procedure. Add about 20 ml. of approximately 0.5 N solution of ammonium salt to a flask which has been roughened with emery, and add 1 drop of a 0.1 per cent solution of rosolic acid. Neutralize with dilute sodium hydroxide and add 30 ml. of a formalin solution which has also been neutralized to rosolic acid. Allow the mixture to stand for 30 minutes, add an equal volume

of neutral ether, and titrate with standard sodium hydroxide solution to a pink color.

(m) Detection of cadmium and zinc. Bey⁶⁷ has recommended the use of an ether solution of resorcinol (page 178) for the detection of cadmium and tin. The sensitivity of the reaction is increased by the collection of the colored compound at the interface of the two liquids.

(n) Determination of selenium. Shibata⁶⁸ recommends the addition of a little ether for the iodometric determination of selenium. This causes the deposited selenium to be adsorbed at the interface of the two liquids.

(o) Determination of gold. Small amounts of gold can be extracted from aqueous solutions with the aid of ether. This is useful, not only for the isolation of gold, but also for separating gold from platinum and palladium.

(p) Separation of rhenium. Rhenium, like molybdenum, may be extracted with ether as the thiocyanate complex.

(q) Determination of bismuth. Bismuth diethyldithiocarbamate may be extracted with ether from a slightly acid solution.⁹⁵

Determination of lithium. Anhydrous lithium chloride is soluble in a mixture of equal parts of alcohol and ether which has been saturated with hydrogen chloride gas. The chlorides of sodium and potassium are practically insoluble in this medium. This method has been used by Rammelsberg⁶⁹ and others⁷⁰⁻⁷⁴ for the separation of lithium from sodium and potassium. For the details of this procedure see section on ethyl alcohol (page 93). Palkin⁷⁵ has used the principle of Rammelsberg but carries out the procedure in an entirely different manner. The dried mixed chlorides are dissolved in a definite minimum of water, the mixture is then acidified with hydrochloric acid, and most of the chlorides of sodium and potassium are precipitated by addition of absolute alcohol, followed by ether.

Separation of sodium and potassium. A mixture of ether and isobutyl alcohol may be used for the separation of sodium and potassium.^{75,76} For details of this see section on isobutyl alcohol (page 107).

Determination of alkaline earth metals. Ether may be used in a procedure for the separation and determination of barium that is associated with strontium.⁷⁷

Procedure. Dissolve the dry mixed chlorides in the least possible quantity of water, warm gently with agitation, and allow to cool. If crystals separate on cooling, cautiously repeat to obtain a clear solution. Then add dropwise a 4:1 mixture of 33 per cent hydrochloric acid and ether. Stir constantly during the addition of the first 2-3 ml. of the precipitant, and then add the mixture in quantities necessary for the complete precipitation of barium chloride and solution of the strontium chloride. Approximately 50-75 ml. is sufficient for quantities of the mixed chlorides not exceeding 0.5 g. and for 0.3 g. anhydrous

strontium chloride. Ether is also used with ethyl alcohol for the separation of calcium and strontium by the method of Rose.^{78,79} For details of this separation, see section on ethyl alcohol (page 95).

Separation of iron and aluminum. Aluminum chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, is virtually insoluble in a mixture of concentrated hydrochloric acid and ether that has been saturated with hydrogen chloride. Ferric chloride is entirely soluble in this medium. This fact has been used by Gooch and Havens⁸⁰ for the separation of iron from aluminum. Palkin⁸¹ has proposed a simpler method based upon the same principle, but in which saturation with hydrogen chloride gas is not essential:

Procedure. Evaporate to dryness on a steam bath a solution containing not more than 0.5 g. of the mixed chlorides of iron and aluminum. Carry out the evaporation in a 150-ml. Erlenmeyer flask and stir the mixture from time to time with a glass rod. Dry in an oven at 120°C . for 30 minutes with occasional stirring as before. Moisten the residue with 0.5-1.0 ml. of absolute alcohol solution containing 25-33 per cent hydrogen chloride. Warm on a steam bath and stir. Add 3-4 ml. of absolute alcohol and heat until solution is complete. Allow to stand until the salts begin to crystallize and add 0.5 ml. of alcoholic hydrogen chloride. Again warm and stir, and then add 30 ml. of U.S.P. ether gradually with stirring. Add 40 ml. of absolute ether with stirring and allow the mixture to stand. Filter through a Gooch crucible, and wash with a solution consisting of 100 parts of absolute ether and 2 parts of alcoholic hydrogen chloride. Ignite and weigh as Al_2O_3 .

Separation of aluminum from beryllium. Aluminum chloride is precipitated when an aqueous solution of the salt is treated with ether and saturated with hydrogen chloride gas. This principle has been used by Havens⁸² for the separation of beryllium and aluminum.

Procedure. To a concentrated aqueous solution containing the chlorides of beryllium and aluminum, add an equal volume of a mixture of equal parts concentrated hydrochloric acid and ether. Saturate the resulting mixture with hydrogen chloride at 15°C ., and add a volume of ether equal to that of the original aqueous solution of aluminum and beryllium. Again saturate with hydrogen chloride and then filter the precipitate of aluminum chloride on asbestos. Wash with a mixture of equal volumes of ether and concentrated hydrochloric acid saturated with hydrogen chloride at 15°C . Dry for 30 minutes at 150°C . and cover with pure mercuric oxide which leaves no residue on volatilizing. Ignite in a hood and weigh as Al_2O_3 .

Churchill and co-workers⁸³ have used a combination of the above method with 8-hydroxyquinoline precipitation for the complete separation of aluminum from beryllium.

Miscellaneous uses. The substitution of ether as an aid in the Volhard titration of silver or chloride for toluene or nitrobenzene has been suggested, but results indicate that it is not as satisfactory as other immiscible liquids^{84,85} (page 60).

Spacu and Spacu⁸⁶ use ether for washing the precipitate of $[\text{AgI}_2]_2[\text{CuPn}_2]$ in the gravimetric determination of silver (Pn = propylenediamine) (see section on propylenediamine). Shemyakin⁸⁷ uses ether as a protective layer in the determination of cerium with gallic acid (see section on gallic acid).

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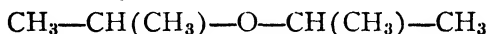
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ISOPROPYL ETHER

$C_6H_{14}O$

Mol. Wt. 102.17

Beil. Ref. I, 362.



Use: Separation of iron.*

Isopropyl ether is a colorless liquid, which boils at 68-69° C. It has a sp. gr. of 0.725. It is slightly soluble in water, but is miscible with alcohol and ether.

Separation of iron. Ferric chloride is frequently extracted from aqueous solutions containing hydrochloric acid by means of ethyl ether. A better separation of ferric chloride is obtained over a wider range of acid concentrations if isopropyl ether is substituted for ethyl ether.^{1,2} The most efficient separation is accomplished by a continuous extraction, carried out in the dark, for 16 hours with isopropyl ether. When the mixture is exposed to sunlight some of the ferric chloride undergoes photochemical reduction.³

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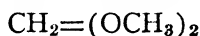
METHYLAL

Synonym: Formaldehyde dimethyl acetal, dimethoxymethane

$C_3H_8O_2$

Mol. Wt. 76.09

Beil. Ref. I, 574.



Use: Detection of ammonia.

Methylal is a clear, volatile, inflammable liquid. It has an odor resembling chloroform. Its sp. gr. is 0.872, and it boils at 41-43° C. It is soluble in 3 parts of water, and is miscible with alcohol and ether.

Preparation: Mix 40 per cent formaldehyde with 1.5 times as much of a 2 per cent solution of hydrochloric acid in methyl alcohol. Add to this solution

an equal quantity of granular (anhydrous) calcium chloride. Allow the mixture to stand for 15 hours and distill. Collect the fraction boiling at 42-43° C.¹

Detection of ammonia. A sensitive test for ammonia is based on the formation of a silver mirror when a solution of methylal and silver nitrate comes in contact with ammonia gas.²

Reagent. Mix 1 ml. of a 20 per cent solution of silver nitrate with 3 ml. of methylal. Heat, before making the test. The reagent is stable only for about 2 hours.

Procedure. To the solution to be tested, add sodium hydroxide until alkaline, and place about 1 ml. of this solution in a 12-ml. test tube. Place a small watch glass on top of the tube. Place a drop of the reagent on a stirring rod and hold near an opening caused by raising the watch glass slightly. Add a little cold water to the top of the watch glass to act as a condenser. Next heat the test tube until drops of moisture begin to condense on the watch glass, and on the rod with the reagent. A silver mirror is obtained with as little as 3.4×10^{-7} g. of ammonia.

Methylal as a solvent. Espil³ has studied the use of methylal as a possible substitute for ether in extraction processes in analytical chemistry, and finds that for certain purposes it can be used advantageously. Aqueous solutions of acetic, lactic, citric, malic, succinic, and tartaric acids can be extracted better with methylal than with ethyl ether.

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CHAPTER XVI

ALDEHYDES

The reducing properties of aldehydes have been used in a number of analytical procedures. These reactions may be based either on the determination of the acid formed by the oxidation of the aldehyde, or upon the character of the reduction product of the unknown substance. For example, ozone may be determined by titrating the butyric acid formed by the oxidation of butyraldehyde, or silver may be detected or colorimetrically determined by the dark color which results from the reduction of silver ions.

A number of aldehydes have been used to reduce post-precipitation during the separation of metals by precipitation with hydrogen sulfide, and formaldehyde has been used for the elimination of ammonia, and for the detection and determination of ammonium salts.

ACROLEIN

Synonym: Acrylic aldehyde, propenal



Mol. Wt. 56.06

Beil. Ref. I, 725.



Use: Separation of zinc from cobalt, manganese and nickel.

Acrolein is a colorless to yellowish, very refractive, inflammable liquid. It has a very pungent odor, and its vapor is very irritating to the eyes and mucosa. The compound melts at -87.5°C . and boils at 52°C . It is soluble in 3 parts of water, and is soluble in alcohol and ether. The reagent is unstable and polymerizes to disacryl, which is a solid.

Preparation: Add 200 g. of anhydrous glycerol to 400 g. of potassium bisulfate, and allow to stand for several days. Distill the mixture from an iron retort. The distillate, which is collected in a well-cooled receiver, separates into two layers. Separate the upper layer, from which the reagent is prepared, and shake with one half its weight of lead oxide to remove sulfurous acid. Distill over anhydrous calcium chloride. Acrolein boils at 52°C .

Separation of zinc and cobalt. Caldwell and Moyer¹ have recently developed a method for the quantitative separation of cobalt and zinc with hydrogen sulfide in one precipitation. Older methods require a number of precipitations for the complete separation of these elements. Acrolein is used to reduce post-precipitation. Other aldehydes are effective, but acrolein is far superior to others that have been tried. Its advantage lies in its specificity of action, and in its low tendency to form a resin.

Aldehydes, and acrolein in particular, are readily adsorbed by the sulfide precipitate, and also react with hydrogen sulfide on the surface of the particles.

This lowers the concentration of the sulfide ion to a point below that required for the precipitation of cobalt sulfide, thus reducing post-precipitation of cobalt on the zinc sulfide.

Procedure. Adjust the pH of the chloride-free solution, containing about 0.25 g. of zinc, so that the hydroxides just remain in solution. Add 6-8 g. of ammonium sulfate, dilute to 250-300 ml., and add 0.2 ml. of acrolein. Pass hydrogen sulfide gas rapidly into the mixture for 30 minutes, and add 5-10 ml. of 0.02 per cent gelatin solution. Allow to stand 15 minutes, filter, and wash with cold water.

Ostroumov² has used acrolein to prevent post-precipitation of cobalt on zinc when the latter is precipitated with anthranilic acid according to the method of Funk and Ditt.³ Post-precipitation is prevented by adding 5 ml. of 4 per cent acrolein solution for each 0.05 g. of zinc oxide.

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BENZALDEHYDE

C_7H_6O

Mol. Wt. 106.12

Beil. Ref. VII, 174.

C_6H_5-CHO

Use: Determination of ozone.

Benzaldehyde is a colorless, strongly refractive liquid, which becomes yellowish on standing. It has the characteristic odor of almond. It oxidizes in air to benzoic acid. It boils at 179° C. and has a sp. gr. of 1.043. Benzaldehyde dissolves in 350 parts of water, but is miscible with alcohol and ether.

Detection of ozone. Like other aldehydes, benzaldehyde is oxidized by ozone to benzoic acid. By means of this reaction ozone can be estimated at concentrations ranging from 10^{-8} to 10^{-6} by passing the gas containing the ozone into a solution of benzaldehyde in carbon tetrachloride. The quantity of ozone present is determined by titrating the benzoic acid formed with an alkali hydroxide.

1. E. Briner and E. Perrottet, *Helv. Chim. Acta.* **20**, 293-8 (1937); *C.A.* **31**, 2957 (1937).

BUTYRALDEHYDE

Synonym: Butanal

C_4H_8O

Mol. Wt. 72.10

Beil. Ref. I, 662.

$CH_3CH_2CH_2-CHO$

Use: Determination of ozone.

Butyraldehyde is a colorless liquid boiling at 75° C. Its sp. gr. is 0.8170 and refractive index is 1.38222. It is soluble in 27 parts of water.

Preparation: Butyraldehyde may be prepared by heating a mixture of 2 molecular weights of calcium formate and 1 molecular weight of calcium butyrate in a retort and fractionating the distillate.^{1,2}

Determination of ozone: Briner and Perrottet³⁻⁶ have used butyraldehyde for the determination of ozone in air. According to this method, air is passed through a solution prepared by dissolving 5 ml. of butyraldehyde in 20 ml. of hexane, whereby aldehyde is oxidized by ozone to butyric acid; the latter is determined by titration with a standard base. The above reagent is reported to work well with ozone concentrations as low as 10^{-8} . The sensitiveness of this reaction is said to be increased by replacing hexane with 2,2,4-trimethylpentane as solvent for the aldehyde.⁶

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CHLORAL

Synonym: Trichloroacetaldehyde



Mol. Wt. 147.40

Beil. Ref. I, 616 (328).



Use: Detection and determination of silver.

Chloral is a colorless, caustic liquid which possesses a pungent odor. It is unstable and unites with water to form chloral hydrate. Its sp. gr. is 1.506, it boils at 98° C. and melts at 57-58° C. It is very soluble in water, alcohol, and ether. Chloralhydrate consists of colorless transparent crystals which have a pungent odor and taste. It melts at about 52° C. and boils at 98° C. with decomposition into chloral and water.

Preparation: Chloral hydrate is obtained by the action of chlorine upon ethyl alcohol. Solid chloral alcoholate is formed, and this is decomposed upon treating with sulfuric acid to form chloral. The latter readily combines with water to form the crystalline hydrate.^{1,2}

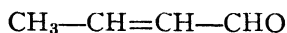
Detection and determination of silver. Metallic silver is formed when chloral hydrate is added to an ammoniacal silver nitrate solution and the mixture warmed. This reaction has been used by Costeanu³ for the detection and semiquantitative estimation of silver. Filter paper is impregnated with a saturated solution of chloral and this is treated with a drop of the ammoniacal silver salt solution. A black spot due to metallic silver appears if silver was present in the unknown. This reaction may be made quantitative by comparing the spot formed with the unknown with that obtained using a standard solution of silver nitrate.

1. J. Liebig, *Ann.* **1**, 189 (1832).
2. Dumas, *Ann. Chim. Phys.* **56**, 123 (1834).
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CROTONALDEHYDE

Mol. Wt. 70.09

Beil. Ref. I, 728.

**Use:** Determination of copper.

Crotonaldehyde is a liquid possessing a pleasant, fruit-like odor. It is a lachrymator. It boils at 102.15° C., melts at -76.5° C., and has a sp. gr. of 0.8477. It is soluble in water and alcohol.

Preparation: Add 50 g. of paraldehyde in portions of 10-15 g. to 250 ml. of concentrated sulfuric acid while cooling with running water. Allow the mixture to stand for 15 minutes, dilute with water to 2 liters, and distill off from the liquid about one tenth of its volume with steam. The distillate is then heated, and the crotonaldehyde passes over in the first portion together with some water. Separate, and pour the aqueous distillate back into the flask, and repeat the process until no more oil comes over.¹

Determination of copper. Crotonaldehyde, like acrolein, is used to reduce post-precipitation of zinc on copper sulfide when the latter is precipitated with hydrogen sulfide from a solution containing both copper and zinc ions. Acrolein, however, appears to be the more satisfactory of the two aldehydes.²

1. M. Delepine, *Compt. rend.* **147**, 1317 (1908).

2. J. R. Caldwell and H. V. Moyer, *J. Am. Chem. Soc.* **59**, 90-2 (1937); *C.A.* **31**, 6580 (1937).

FORMALDEHYDE

Synonym: Methanal, formalin



Mol. Wt. 30.03

Beil. Ref. I, 558.



Use: Detection of ammonia, ammonium salts, bismuth, bromine, cadmium, chlorine, colloids, copper, germanium, gold, nickel, nitrate, silver, sulfite, and thiocyanate.

Determination of ammonium salts, bismuth, bromate, bromine, chlorate, chlorine, copper, germanium, gold, hydrazine sulfate, iodate, iodine, mercury, nickel, periodate, silver and thiocyanate.

Formaldehyde is a gas at ordinary temperatures. It is very soluble in water, and is usually used in aqueous solution. A solution containing about 37 per cent of the gas dissolved in water, and containing about 10-15 per cent alcohol to prevent polymerization, is the familiar laboratory reagent. This solution is of the same strength as that known as formalin 40 per cent, which indicates that the mixture contains 40 g. of the gas in 100 ml. of solution. This is equivalent to 37 per cent by weight.

This solution is a colorless liquid possessing a pungent odor. Its vapors are highly irritating to the mucous membranes. On standing, particularly in the

cold, the solution may become cloudy, and at very low temperatures a precipitate of trioxymethylene is formed. The compound is a powerful reducing agent, particularly in the presence of an alkali. In air it slowly oxidizes to formic acid. The solution is miscible with water, alcohol, and acetone.

Detection of ammonia. Zenghelis¹ Feigl,² and Duval³ have described a procedure whereby ammonia and ammonium salts may be detected by the formation of a silver mirror with the aid of formaldehyde and silver nitrate. The following procedure has been proposed by Duval:

Procedure. Mix a drop of the sample with a drop of 2 N sodium hydroxide in a 5 × 18 mm. test tube, cover with a glass plate, and heat on a sand bath to 40° C. The ammonia gas rises in the tube and reacts with a drop of a reagent prepared by gradually adding 0.04 ml. of 40 per cent formalin to 1 ml. of 20 per cent aqueous silver nitrate. This drop is placed on the underside of the cover glass, and with ammonia forms a silver mirror. The formation of the mirror is observed by reflection of a strong beam of light. A drop of water on the upper side of the glass plate acts as a cooling agent and as a lens to observe the silver mirror. The addition of a little cupric nitrate to the reagent makes the mirror firmer. As little as 0.003% of ammonia can be detected by this method.

A different procedure has been used by Kollo and Teodossiu.⁴

Procedure. Mix a drop of formaldehyde with an equal quantity of 1 per cent picric acid, and expose the mixture to the gas suspected of containing ammonia. In the presence of ammonia, urotropine is formed, and this combines with the picric acid to form prismatic yellow crystals.

Detection of ammonium salts. Formaldehyde reacts with ammonium ions according to the following equation:



The hydrogen ions produced in this reaction may be detected with the aid of phenolphthalein, thereby serving indirectly as an indication of the presence of ammonium ions in an unknown solution.⁵ A test based on this reaction may be carried out as follows:

Procedure. Add several drops of 1 per cent phenolphthalein solution to 1-2 ml. of the solution to be tested, and then carefully add a dilute solution of sodium hydroxide until a red color appears. If colored hydroxides are precipitated, filter, and carefully neutralize the red filtrate with dilute hydrochloric acid to a pink color. Add, drop by drop, a weak alkaline solution of formaldehyde. If ammonium ions are present, the solution becomes colorless. As little as 10⁻⁶ g. of ammonium ion in 1 ml. can be detected by this method. In the presence of other ions, the sensitiveness of this reaction is reduced somewhat.

Determination of ammonium salts. Ammonium salts may be determined volumetrically by titrating the acid formed when ammonium ions react with

formaldehyde. The equation for the reaction shows the relation between ammonium and hydrogen ions:



This, the so-called "formol titration," was devised by Sørensen.^{6,7,89} Malfatti¹¹ and Ronchese⁸ have found this method to be satisfactory, but van Bers⁹ claims that the direct titration of the liberated acid gives unsatisfactory results. Kolt-hoff¹⁰ states that satisfactory results can be obtained by the direct titration of the acid, provided a sufficient excess of water is used and the mixture is allowed to stand for 1 minute before titration. The following procedure by Kolthoff¹⁰ is typical of several proposed by various investigators.¹²⁻¹⁸

Procedure. For pure ammonium salts: to 25 ml. of approximately 0.1 M solution, add 5 ml. of formalin, previously neutralized to phenolphthalein, and then 2-3 drops of 1 per cent phenolphthalein and stir. Allow to stand for 1 minute, and titrate the mixture with 0.1 N alkali to a faint rose color. One ml. of 0.1 N alkali = 1.8 mg. NH_3 . If the ammonium salt is not neutral to methyl red, it must first be neutralized.

Sorrentino¹⁸ has used 0.2 N barium hydroxide for the titration, and claims good results. Urea, dicyandiamide, and guanidine do not interfere.

Shaw¹⁹ used the formol titration in connection with the Kjeldahl determination of nitrogen. According to this method, the distillation procedure is unnecessary, thereby eliminating a time-consuming operation.

Gaillot²⁰ has proposed a method for determining ammonia which is based upon the formation of insoluble hexamethylenetetramine with formaldehyde, but Pozzi-Escot²¹ claims that the hexamethylenetetramine is not insoluble under the conditions used in the determination. According to Pozzi-Escot, the method of Gaillot should be discarded, since it is not as accurate as a distillation method.

Elimination of ammonia and ammonium salts in analysis. Formaldehyde is very useful for the elimination of ammonia and ammonium salts in qualitative and quantitative analysis. Many procedures require the absence of ammonium salts for their successful completion, and this can be realized by converting the ammonium ion to hexamethylenetetramine with formaldehyde.²²⁻²⁵

Determination of hydrazine sulfate. Ammonium salts, amino acids, and hydrazine sulfate can be titrated with a formaldehyde solution, using methyl red as an indicator. If considerable alcohol is added, and phenolphthalein is used as the indicator, twice as much aldehyde is required as with methyl red.²⁶

Elimination of cyanides. Formaldehyde reacts with alkali cyanides to form the alkali compound of the nitrile of glycolic acid. In this way cyanide ions may be removed from solutions where their presence might be undesirable. This reaction has been used for the detection of cadmium by means of dinitrodiphenylcarbazine²⁷ (see section on dinitrodiphenylcarbazine).

Conflicting statements have appeared in the literature concerning the reaction which takes place when formaldehyde and potassium cyanide react. According to Mutschin⁵⁹ the primary product is $\text{CN}-\text{CH}_2\text{OK}$ as Romijn first assumed in

1897. Under certain conditions this compound may be converted into $\text{CH}_2\text{OH}-\text{CO}_2\text{K}$ and hexamethylenetetramine.

Detection of copper and nickel. Nickel and copper may be detected by means of color reactions obtained with a mixture of formaldehyde and hydroxylamine hydrochloride.^{28,29}

Reagent. Mix equal quantities of 20 per cent formaldehyde and hydroxylamine hydrochloride.

Procedure. Add 0.5 ml. of the reagent and 0.5 ml. of 15 per cent potassium hydroxide solution to 15 ml. of the solution to be tested. Copper salts produce a violet color at concentrations as low as 1 mg. per liter. Nickel salts give an orange-yellow color.

Iron salts interfere with this reaction.

Stea has claimed that the addition of a solution of soap and formaldehyde to copper salts produces a green coloration which is characteristic for copper. Giorgio³⁰ has used this reaction, and reports that all metals except the alkalis give similar precipitates, and that the reagent is of little or no interest for detecting copper.

Determination of copper. Hersch³¹ has determined copper by reduction of copper salts to the metal from alkaline tartrate solutions (Fehling's solution). This reaction was first described by Loew,³² and was later used by Hartwagner.³³

Procedure. To the neutral solution containing 0.3-0.4 g. of copper, add 8-10 ml. of 20 per cent Rochelle salt solution, 30 ml. of 10 per cent sodium hydroxide solution, and 3 ml. of 40 per cent formaldehyde. Dilute the mixture to 100 ml. and transfer to a weighed platinum dish. Allow to stand 2-3 hours until most of the copper is deposited as an adherent film on the dish. Heat in an oven at 50° C. until the solution is colorless. Wash the film with water, and then with methyl alcohol, and finally weigh.³¹

Hemmeler³⁴ uses a somewhat similar method. According to this method, about 0.2 g. of the copper compound and 2-3 g. of hexamethylenetetramine are boiled together, the mixture filtered, washed, and the precipitate ignited to constant weight as copper oxide. To determine copper in an ammoniacal solution, simply add an excess of formaldehyde solution and proceed as above after boiling the solution to expel the excess formaldehyde. Copper sulfate yields better results than the chloride or nitrate, since some copper is lost when the latter compounds are ignited.

The precipitation of copper with formaldehyde makes possible the separation of copper from manganese, magnesium, cadmium, nickel, cobalt, the alkali metals, and the alkaline earths. It is difficult to separate zinc or silver.

Copper may be determined volumetrically by using a solution prepared by passing sulfur dioxide into a 40 per cent solution of formaldehyde.³⁵ The titration is carried out in an ammoniacal solution, and the end-point occurs when the solution changes from blue to colorless.

Detection and determination of nickel in the presence of cobalt. Nickel may be detected or determined with dimethylglyoxime in the presence of cobalt with the aid of formaldehyde and potassium cyanide. Bivalent nickel and cobalt are converted to $\text{Ni}(\text{CN})_4^{-2}$ and $\text{Co}(\text{CN})_6^{-3}$ by potassium cyanide, and the nickel complex is then converted to the nickel ion and $\text{CN}-\text{CH}_2-\text{OK}$ by the action of 2 molecules of formaldehyde. Nickel is then detected or determined with dimethylglyoxime. The cobalt complex is more stable and is not decomposed with formaldehyde.³⁶

Procedure. Dissolve 0.5-1.0 g. of a cobalt salt containing a little nickel (or a mixture containing nickel) in 2-3 ml. of water, and treat with concentrated potassium cyanide solution until the precipitate which first forms just dissolves. Add hydrogen peroxide to the hot solution until a honey-yellow color shows the presence of $\text{Co}(\text{CN})_6^{-3}$. Evaporate the solution until the volume is small, and add an excess of dimethylglyoxime. To the warm solution (50° - 60° C.) add formaldehyde solution until an excess is indicated by the odor. Shake with 1-2 ml. of ether. The precipitate may be weighed for the determination of nickel.

Detection of cadmium in the presence of copper. Formaldehyde is used to detect cadmium in the presence of copper. This method is similar to that employed for the detection of nickel in the presence of copper. The reagent is dinitrodiphenylcarbazide.²⁷ The cadmium cyanide complex is decomposed by formaldehyde, and the resulting cadmium ions are precipitated as cadmium hydroxide in the presence of dinitrodiphenylcarbazide. The copper cyanide complex is more stable and is not decomposed.

Determination of mercury. Small quantities of mercury may be determined by precipitating mercury from solutions of its salts. The mercury is dissolved in 0.02 N iodine solution, the mixture heated to 100° C. to remove the excess iodine, and the combined iodine in the form of mercuric iodide is determined by the method of Bernier and Peron,^{67,68} using potassium permanganate, or by conversion to the iodate with bromine, followed by titration with 0.02 N sodium thiosulfate after adding potassium iodide and acetic acid.³⁷

Detection of bismuth. Louw³⁸ has proposed a revised Nylander test for bismuth, using formaldehyde instead of glucose for the reduction of the bismuth salts. The sensitiveness of this reaction is 1:100,000.

Determination of bismuth. Bismuth may be determined by reducing compounds of this element to the metal with an alkaline solution of formaldehyde.^{39,40} The following procedure may be used:

Procedure. To a weakly acid solution of a bismuth salt, add formaldehyde and a strong excess of 10 per cent sodium hydroxide, and warm on a water bath with shaking. Add an additional quantity of formaldehyde and sodium hydroxide, and heat for a time over a free flame. Wash the residue by decantation, transfer to a Gooch crucible, wash with absolute alcohol, dry at 105° C. and weigh.

Detection and determination of silver. Silver may be detected by reducing an alkaline solution of a silver salt with formaldehyde. The use of this reaction is illustrated by the procedure of Van Atta:⁴¹

Procedure. To the solution suspected of containing silver, add dilute hydrochloric acid to form insoluble silver chloride. Treat the precipitate of the chloride with ammonia, and to the ammoniacal solution so formed add 5 drops of 20 per cent potassium hydroxide and 2 drops of 40 per cent formaldehyde. A precipitate of finely divided silver is a positive test.

This reaction may also be used for the determination of silver.⁴²

Procedure. Boil a solution of silver nitrate with a slight excess of formaldehyde in 15 per cent ammonium hydroxide solution, wash the precipitated silver, and ignite at 450-500° C.

Results obtained by this method agree with those in which silver is precipitated as the chloride within 0.005 per cent.

Silver may also be detected in a solution of concentration of 1:240,000 by the color of a colloidal solution obtained by the reduction of a silver salt with a solution prepared by mixing 2 volumes of 40 per cent formaldehyde and 1 volume of 20 per cent potassium hydroxide.⁴³

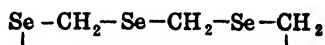
An interesting semi-quantitative method for determining silver has been used by Costeanu.⁴⁴ Filter paper is impregnated with an alkaline solution of formaldehyde, a drop of the solution to be analyzed is placed on this paper, and the quantity of silver present is estimated from the appearance of the spot formed by the reduction of the silver salt. A series of comparison spots prepared from solutions of known silver content is used.

Detection and determination of gold. Gold may be detected in a solution of concentration 1:100,000 by the color of the colloidal solution obtained by reducing the gold salts with a reagent prepared by mixing 2 volumes of 40 per cent formaldehyde and 1 volume of 20 per cent potassium hydroxide.⁴⁵ This color may also be used for the determination of small quantities of gold.⁴⁵ The presence of heavy metals and certain electrolytes, however, interferes with this color test.⁴⁶

Spot tests, from which an indication of the gold content of solutions may be obtained, may be made by using filter paper which has been impregnated with an alkaline solution of formaldehyde.^{47,48}

Isabisi and Singawa⁴⁹ have determined gold in sea water by reducing with formaldehyde, followed by dialysis and cupellation.

Detection and determination of germanium. When hydrogen selenide is added to an aqueous solution of formaldehyde, a fairly stable derivative is formed which reacts with germanium to form a yellow precipitate. The composition of the hydrogen selenide-formaldehyde derivative is probably



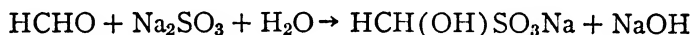
The reaction between this compound and germanium may be used as a fairly sensitive test for germanium.⁵⁰ The test is carried out as follows:

Reagent. Heat gently 20 g. of selenium with 20 g. of sodium chloride and 14 g. of aluminum. Decompose the aluminum selenide with water and absorb the resulting hydrogen selenide in a solution of formaldehyde. This solution becomes turbid after 2 days, even in the absence of germanium.

Procedure. Add 3 drops of the above solution to 5 ml. of the germanium solution and 1 ml. of concentrated hydrochloric acid. A yellow turbidity or precipitate appears if germanium is present. The sensitivity of this test is 1:5,000,000. In the presence of an excess of arsenic, tin, selenium, and other elements, the following procedure is recommended:

Procedure. Add a few drops of 2 N potassium fluoride to the solution to be tested, and add the formaldehyde-hydrogen selenide reagent. In the presence of fluoride ions, germanium precipitates very slowly. Filter and add a little aluminum sulfate. The aluminum ions combine with the fluoride ions to form the aluminum fluoride complex ion, and with the removal of the fluoride ions in this way, the remainder of the germanium is precipitated.

Detection of sulfite. Sulfites may be detected in a solution neutral to, and containing phenolphthalein by adding a few drops of 1 per cent formaldehyde. A red color appears in the presence of sulfites due to the formation of an alkali hydroxide. This is shown in the following equation:



A distinct rose color is produced by as little as 0.1 mg. of sulfite in 0.5 ml. of a 0.1 N thiosulfate solution.⁵¹

Analysis of a mixture of sulfide, sulfite, and thiosulfate. The compound formed when formaldehyde reacts with sodium bisulfite is so stable that it does not react with iodine. Thus, when sulfites and other substances which are capable of reacting with iodine are present in a solution to be analyzed, the sulfite can be advantageously removed by the addition of formaldehyde.⁵² Sulfide ions react slowly with formaldehyde to form a compound which is only slowly oxidized by iodine, and so it is necessary to precipitate sulfides from a mixture as zinc sulfide.⁵³ From the above it may be seen that thiosulfates can be determined iodometrically in a mixture with sulfides and sulfites by first adding formaldehyde and precipitating the sulfide with a solution of a zinc salt.^{54,55}

Detection and determination of chloride, bromide, and thiocyanate in the presence of the other halides and cyanides. A mixture of 1 part of 40 per cent formaldehyde and 10 parts of 0.1 N sodium hydroxide added to freshly washed precipitates of silver chloride, silver bromide, and silver iodide reduces only the chloride to free silver. A slight darkening of the precipitate does not necessarily prove the presence of silver chloride, since it is extremely difficult to remove the last traces of silver nitrate (used in the precipitation) from the

halide precipitate. In case of doubt, the presence of chloride in the alkaline filtrate from the formaldehyde treatment may be shown by acidifying with a little nitric acid and adding a few drops of silver nitrate solution.⁵⁶

The total halogen and thiocyanate content of a mixture of salts containing cyanides may be determined with the aid of formaldehyde.^{57,58}

Procedure. Dissolve 0.1-0.3 g. of a mixture of the salts to be analyzed in 50 ml. of water, and add 5 ml. of 20 per cent formaldehyde. Shake well, add 5 ml. 30 per cent nitric acid, and titrate the total halogen content by the Volhard method.

The hydrogen cyanide is converted to the nitrile of glycolic acid and hexamethylenetetramine.

Mutschin⁵⁹ has used a method similar to that described above for determining chlorides, bromides, and iodides in the presence of cyanides by Mohr's method employing adsorption indicators.

Determination of iodides. Formaldehyde has been used in a titration method for the determination of small quantities of iodides.⁶⁰ The following procedure illustrates this use:

Procedure. Dilute a solution containing 0.01-0.04 g. of iodide to 30 ml. Make slightly acid with hydrochloric acid, and add bromine-water (1 g. of bromine in 100 ml. of water) drop by drop until the solution is pale yellow in color. Shake well, allow to stand for 10 minutes, and add 2 ml. of 40 per cent formaldehyde solution. Then add a solution of sodium hydroxide dropwise until the solution is decolorized. Allow to stand 5 minutes, add 5 ml. of glacial acetic acid and 5 ml. of a solution of potassium iodide, and titrate the liberated iodine with sodium thiosulfate, using starch as indicator.

Determination of chlorate, bromate, iodate, and periodate. Chlorates, bromates, iodates, and periodates may be determined by reduction in the presence of formaldehyde and potassium persulfate, followed by precipitation as the corresponding silver halide.^{61,62}

Procedure. Add 5 ml. of nitric acid ($d = 1.2$) to 0.2 g. of the material to be analyzed dissolved in 20 ml. of water, and add 0.3 g. of silver nitrate and 3 g. of potassium persulfate. Heat the mixture to 80-90° C. and add formaldehyde until the silver halides are completely precipitated. Add 5 ml. of alcohol to aid in the precipitation. The halide may be weighed or determined volumetrically by substituting N/10 silver nitrate for the solid salt, and titrating the excess with standard thiocyanate solution.

Detection of nitrates. Fulton⁶³ has proposed a test for nitrates employing formaldehyde. If a little nitrate is mixed with concentrated sulfuric acid, and a drop of concentrated formaldehyde is added, the addition of a little 20 per cent copper sulfate solution causes the appearance of a deep-violet color. If no nitrate is present, the color is pale blue. A brown color is formed if a 0.5 per cent solution of chloroauric acid is used instead of 20 per cent copper sulfate. A deep-red color is obtained if ferric chloride is used.

Reagent for colloids. A red colloidal gold solution, prepared by reducing gold chloride with formaldehyde in the presence of dilute alkali, is used for the classification of colloids.⁶⁴⁻⁶⁶ This reagent turns blue when mixed with sodium chloride because of the agglomeration of gold particles, but this change of color is prevented by the presence of a sufficient quantity of certain colloids. Thus, colloids may be classified according to the amount required to prevent this color change. This is the basis for the so-called *gold number* of a colloid.

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FURFURALDEHYDE

Synonym: Furfural, pyromucic aldehyde, furfurol

$C_5H_4O_2$

Mol. Wt. 96.08

Beil. Ref. XVII, 272.

C_4H_3O-CHO

Use: Detection of cobalt.

Determination of sulfate.

Furfuraldehyde is a colorless liquid which, on exposure to air, quickly turns to yellow and brown, and finally forms a resin. The liquid boils at 162° C., and has a sp. gr. of 1.159. It is soluble in 11 parts of water, and is very soluble in alcohol and ether.

Preparation. Place 300 g. of bran in a 3-liter flask, and stir with a mixture of 150 ml. of concentrated sulfuric acid and 800 ml. of water. Distill approximately 900 ml. of the liquid, neutralize the distillate with sodium carbonate, and saturate with common salt (250 g.). Distill approximately 300 ml. of this liquid, saturate the distillate with salt, and extract with ether. Dry the ether extract, and evaporate the ether. The furfuraldehyde is then distilled. Collect the fraction boiling at 162° C.¹

Detection of cobalt. Nitrate and furfuraldehyde in a saturated solution of ammonium thiocyanate give a green color which is perceptible in 16,000 parts of water. Iron interferes, and if present must be removed with sodium pyrophosphate. Bismuth interferes if present in large quantities.²

Colorimetric determination of sulfate. In the presence of dilute hydrochloric acid, alcohol and a constant quantity of furfuraldehyde, a yellow color is obtained with benzidine. Using this reaction, Yamazaki³ has developed a method for determining the benzidine content of a benzidine sulfate precipitate. In this way sulfates may be determined indirectly.

Procedure. To 5 ml. of the solution to be analyzed in a test tube, add 2 drops of 0.04 per cent bromophenol blue, and then N hydrochloric acid until a pure yellow color is obtained. Add 5 ml. of water and 2 ml. of 0.025 N benzidine hydrochloride solution and 5 ml. of 90 per cent acetone to insure complete precipitation. Filter, and wash the residue 3 times with small quantities of 90 per cent acetone. Dissolve the precipitate in 15 ml. of 0.02 N sodium hydroxide in 50 per cent alcohol. To this solution add 10 drops of 10 per cent barium chloride solution, make acid to phenolphthalein and add 10-15 drops of N hydrochloric acid in excess. Finally, dilute to exactly 15 ml., mix well, and to 5 ml. of this solution add 2 ml. of pure 1 per cent aqueous furfuraldehyde solution. Compare the resulting color with that of solutions containing known quantities of benzidine similarly prepared.

This method has been used with fairly good results in determining sulfates in urinalysis. Considerable quantities of chlorides cause low results, and the presence of phosphoric acid causes values that are too high.

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***o*-NITROBENZALDEHYDE**

$C_7H_5O_3N$

Mol. Wt. 151.12

Beil. Ref. VII, 243.



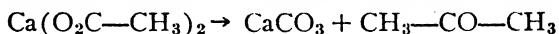
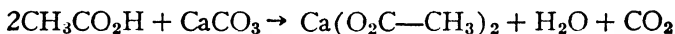
Use: Detection of acetate.

o-Nitrobenzaldehyde consists of bright yellow needles which melt at 43.5-44.5° C. It is slightly soluble in water and is soluble in most organic liquids.

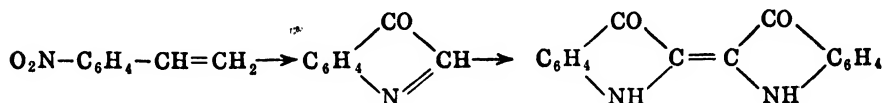
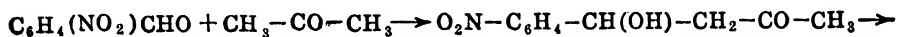
Preparation: Mix 90 g. of acetic anhydride, 30 g. of glacial acetic acid, 15 g. of sulfuric acid, 10 g. of *o*-nitrotoluene and 10 g. of chromic acid at 5-12° C. Allow the mixture to stand for 6-7 hours after the addition of the chromic acid. Extract the resulting diacetate with ether and crystallize from

acidified extract. *o*-Nitrobenzaldehyde is obtained by boiling the diacetate with a mineral acid.¹

Detection of acetate. Calcium acetate is formed when acetic acid is treated with calcium carbonate, and acetone is formed by the dry distillation of the resulting calcium salt.



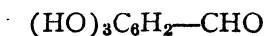
Indigo, a blue compound, is formed when acetone is allowed to react with *o*-nitrobenzaldehyde.



Consequently, the conversion of acetic acid to calcium acetate, and the subsequent formation of acetone may be used as the basis for an indirect test for acetates.^{2,3} The acetone vapor formed in the reaction is allowed to come in contact with paper impregnated with *o*-nitrobenzaldehyde and is detected by means of the blue color which appears. Acetone vapor reacts only slowly and incompletely at ordinary temperatures, but the vapor produced by distillation of calcium acetate is warm enough to cause a rapid conversion to indigo. This reaction is not specific for acetone but is obtained with other compounds containing the $\text{CH}_3\text{CO}-$ group. Propionic acid and other acids of this series do not interfere since their calcium salts yield upon distillation ketones which do not contain the $\text{CH}_3\text{CO}-$ group.

Procedure. Mix a solid sample of the acetate with a little calcium carbonate, or evaporate a drop of the solution of the acid to dryness with calcium carbonate, and transfer the residue to a hard glass tube. Cover the open end of the tube with a strip of filter paper moistened with a freshly prepared, saturated solution of *o*-nitrobenzaldehyde in 2 N sodium hydroxide. Keep the filter paper in place with a small cover glass. Suspend the tube through an asbestos plate and heat gently to volatilize the acetone. The yellow paper is colored blue or blue-green depending upon the amount of acetate originally present. If only small quantities of acetate are present, remove the filter paper after the distillation and treat with a drop of hydrochloric acid. The original yellow color of the paper is bleached by the acid treatment, and the blue color of the indigo may be more plainly seen. By this test 60% of acetic acid may be detected.

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PYROGALLOLALDEHYDE Synonym: 2,3,4-Trihydroxybenzaldehyde $C_7H_6O_4$ Mol. Wt. 154.12 Beil. Ref. VIII, 388(684).

Use: Detection of thorium and zirconium.

Pyrogallolaldehyde is obtained as needle-like crystals from water. These melt at 157-158° C.

Preparation: Pyrogallolaldehyde is prepared by condensing a solution of 38 g. of pyrogallol and 36.3 g. of formanilide in anhydrous ether with 15.2 g. of $POCl_3$, and filtering after 12 hours. The product is crystallized from alcohol to which salt has been added, and the crystals are then suspended in hot sodium hydroxide solution through which a current of hydrogen is passed. Acidify, extract the aldehyde with ether, and purify by forming the bisulfite compound.

Detection of thorium and zirconium. Solutions of thorium and zirconium compounds yield a yellow coloration when treated with pyrogallolaldehyde.^{1,2} This color changes slowly on standing or immediately on boiling, or on the addition of hydrogen peroxide, to a dirty-yellow precipitate and a colorless solution. A solution containing only 0.1 mg. of thorium nitrate in 100 ml. shows this color clearly.

With cerous compounds a brownish yellow color is obtained but no precipitate, even on boiling. On the addition of nitric, sulfuric, or hydrochloric acid the color is discharged.

1. H. Kaserer, *Chem.-Ztg.* **42**, 291 (1918); *C.A.* **13**, 3111 (1919).

2. H. Kaserer, *Chem.-Ztg.* **42**, 170-1 (1918); *J. Soc. Chem. Ind.* **37**, 352A; *C.A.* **12**, 2174 (1918).

SALICYLALDEHYDESynonym: *o*-Hydroxybenzaldehyde $C_7H_6O_2$ Mol. Wt. 122.12 Beil. Ref. VIII, 31.

Use: Detection of copper and nickel.

Determination of copper and nickel.

Salicylaldehyde is a clear, colorless, oily liquid. It has a bitter almond-like odor and a burning taste. It boils at 196-197° C. and has a sp. gr. of 1.167. It is only slightly soluble in water, but is soluble in alcohol and ether.

Preparation: Dissolve 80 g. of sodium hydroxide in 80 ml. of water by heating and add 25 g. of pure phenol to the hot solution. Cool to 60-65° C. by immersing the flask in cold water, but avoid shaking. Close the flask with a two-holed cork fitted with a reflux condenser and thermometer. The bulb of the thermometer should dip into the liquid. Add 20 g. of chloroform through the condenser and shake the mixture gently. Keep the temperature at 65-70° C.

for 10 minutes by dipping the flask in hot or cold water as necessary, and add a second 20-g. portion of chloroform. Keep at 65-70° C. for an additional 15 minutes and add a third 20-g. portion of chloroform. Shake the flask frequently during this addition. Heat the flask on a water bath for an hour, and then distill with steam. When all chloroform has passed over, cool somewhat, and add dilute sulfuric acid carefully until the orange-colored, alkaline liquid becomes acid and almost colorless. Again steam distill until no more drops of oil come over.

Extract the distillate immediately with ether and heat the extract on a water bath until most of the ether is removed. Shake the residue vigorously in a glass-stoppered bottle with 2 volumes of concentrated sodium bisulfite solution. Allow the mixture to stand for 1 hour and filter with suction. Wash several times, first with alcohol and finally with ether until the residue is free of phenol. Mix the crystals with dilute sulfuric acid in a small flask which is fitted with an air condenser and warm gently on a water bath. Cool, extract the aldehyde with ether, and dry the ether solution with anhydrous sodium sulfate. The pure aldehyde which remains distills at 196° C.¹

Detection and determination of nickel and copper. In 1840, Ettling² found that salicylaldehyde yields insoluble compounds when treated with ammoniacal cupric, nickel or ferric ions. Schiff³ showed that compounds obtained are complexes of the ion with salicylimine, $C_6H_4(OH)CH=NH$, which is formed by the reaction of the aldehyde and ammonia. Pfeiffer, Buchholz and Bauer⁴ prepared a number of salicylimine complexes and studied their properties. Primary amines may be used to replace ammonia and form N-alkyl salicylimine complexes.

Recently Duke⁵ has studied the reactions of salicylimine with various cations to determine its applicability in analytical procedures. The ions which give reactions are listed in Table 60.

TABLE 60.—REACTIONS OF SALICYLALDEHYDE IN AMMONIACAL SOLUTION

Ion	Reaction	Ion	Reaction
Cupric	Green precipitate	Palladous	Yellow precipitate
Nickel	Orange precipitate	Ferric	Red precipitate
Vanadyl	Red precipitate	Ferrous	Red color

No other common ions give perceptible reactions. Nickel and copper are quantitatively precipitated. All reactions are carried out in the presence of 5 per cent sodium tartrate to prevent precipitation of the hydrous oxides. Since all metal salicylimine derivatives are unstable in the presence of even weakly acid solutions, the pH of the solution must be adjusted to 8-12 before precipitation with the reagent.

The test for copper or nickel is made as follows:

Reagent. Dissolve 1 g. of salicylaldehyde in 100 ml. of 1:9 ammonium hydroxide.

Procedure. Add a little of the solution to be tested to 5 ml. of 5 per cent sodium tartrate solution and add 2 ml. of the reagent. A green precipitate forms with copper and an orange precipitate with nickel. The test may be made more sensitive by comparing with a blank. The test is sensitive to 1 part of the ion in 2,000,000 parts of solution.

Nickel and copper may be determined by the following procedure:

Reagent. Dissolve 1 g. of salicylaldehyde in 100 ml. of 1:9 ammonium hydroxide.

Procedure. Add sodium tartrate to the unknown solution until the concentration is 5 per cent, and then make distinctly alkaline with filtered ammonium hydroxide. Cool below 25° C. and add an excess of salicylimine reagent. Allow to stand for 5 minutes and filter through a glass filtering crucible. Dry to constant weight at 100° C. (never above 105° C.). The factor for copper is 0.2092 and for nickel 0.1963.

Results obtained using this method are shown in Table 61.

TABLE 61.—DETERMINATION OF COPPER AND NICKEL
WITH SALICYLIMINE

Copper Taken mg.	Nickel Taken mg.	Wt. of Ppt. mg.	Copper Found mg.	Nickel Found mg.
9.85	46.9	9.81
9.85	47.1	9.85
24.87	118.6	24.81
24.87	118.6	24.81
49.58	236.9	49.56
49.58	236.6	49.50
.....	8.91	44.9	8.81
.....	8.91	45.1	8.85
.....	22.57	115.4	22.65
.....	22.57	115.2	22.61
.....	44.78	227.6	44.68
.....	44.78	228.0	44.76

The 5-nitro, 5-bromo and 3,5-dibromo derivatives of salicylaldehyde have also been studied as reagents for nickel and copper, and also their corresponding N-methyl inines, and they have been found to give essentially the same results as salicylaldehyde.

Detection of scandium. An intense yellow color is obtained when *o*-aminobenzene arsonic acid and salicylaldehyde are added to an acetic acid solution of a scandium salt. The sensitivity of this reaction is 1:2,000,000. Other elements of the third group of the periodic table do not give this color.

but color reactions are obtained with all elements precipitated by arsonic acids. Titanium and thorium give colors as bright as that with scandium. Only *o*-amino-arsonic acids and *o*-hydroxyaldehydes yield compounds capable of this reaction.⁶

1. Reimer and Tiemann, *Ber.* **9**, 423, 824 (1876) ; **10**, 1562 (1877) ; **15**, 2685 (1882).
2. C. Ettling, *Ann. Chem.* **35**, 265 (1840).
3. H. Schiff, *Ann. Chem.* **150**, 197 (1869).
4. P. Pfeiffer, E. Buchholz and O. Bauer, *J. prakt. Chem.* **129**, 163 (1931).
5. F. R. Duke, *Ind. Eng. Chem., Anal. Ed.* **16**, 750-1 (1944) ; *C.A.* **39**, 673 (1945).
6. V. I. Kuznetsov, *J. Gen. Chem. (U.S.S.R.)* **14**, 897-901 (1944) ; *C.A.* **39**, 4810 (1945).

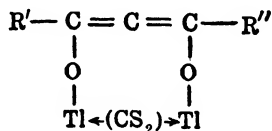
CHAPTER XVII

KETONES

An acidic enol-group may be formed by the migration of a hydrogen atom from some part of a ketone molecule to a carbonyl group, and thus impart to the molecule salt-forming properties. Acetone, which is the most important ketone employed in analytical procedures, is generally used because of its solvent properties, but that it may have acidic properties is indicated by the formation of precipitates with acid solutions of mercuric chloride.

Carbon disulfide reacts with thallium acetylacetonate in an inert solvent to yield an orange-red precipitate or a yellow coloration. Kurowski¹ reports that this reaction permits the detection of 1 g. of carbon disulfide in 1 liter of benzene. A study of the reactions of numerous other diketones with thallium carbonate and carbon disulfide, or of the thallium enolates of diketones with carbon disulfide in inert solvents reveals that colored compounds are produced only with 1,3-diketones having the group $\text{—CO—CH}_2\text{—CO—}$. The reaction is not affected by the character of the radicals attached to this group, but compounds containing thallium are not formed if one or both of the hydrogen atoms of the methylene group are replaced by organic radicals.

The compounds of carbon disulfide and the thallium enolates are stable toward acids and bases, and analysis shows that all contain 2 atoms of thallium and 1 molecule of carbon disulfide to each equivalent of the diketone. These compounds are represented by the following formula



The double enolization of the methylene group is indicated by the fact that compounds of the above type are not formed if one or both of the methylene hydrogen atoms are replaced by radicals.

Compounds containing the $\text{—CO—CH}_2\text{—CO—}$ group may be regarded as specific reagents for thallium in the presence of carbon disulfide, but owing to their low sensitivity they are of little analytical value. It is to be hoped that perhaps the sensitivity of this reaction may be improved.

An interesting example of the stabilization of abnormal types of compounds by complex formation is afforded by the study of the reaction of the thallium enolates with carbon disulfide. Diketones which normally form only mono-enol salts, such as $\text{CH}_3\text{—(OTl)=CH—CO—CH}_3$, yield dienolates through the formation of complex salts.

1. E. Kurowski, *Ber.* **43**, 1079 (1910).

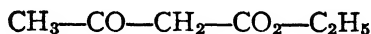
ACETOACETIC ACID ETHYL ESTER

Synonym: Ethyl acetoacetate

 $C_6H_{10}O_3$

Mol. Wt. 130.14

Beil. Ref. III, 632.

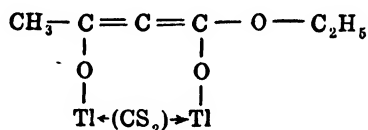
**Use:** Detection of thallium.

Determination of calcium oxide and hydroxide and copper.

Acetoacetic acid ethyl ester is a colorless to slightly yellowish liquid possessing a characteristic odor. It boils at $181^\circ C$. with decomposition, and has a sp. gr. of 1.026-1.028. It is soluble in about 35 parts of water, and is miscible with alcohol, benzene, chloroform and ether.

Preparation: Acetoacetic acid ethyl ester is prepared by the action of metallic sodium on ethyl acetate.^{1,2}

Reaction with thallium and carbon disulfide. Acetoacetic acid ethyl ester does not yield a thallium compound similar to those of other enolic compounds, but with thallium carbonate and carbon disulfide a yellow compound, having the formula $C_7H_8O_3S_2Tl_2$ is formed. This compound probably has the following structure:^{3,4}



Determination of calcium oxide and calcium hydroxide. Calcium oxide and calcium hydroxide may be determined in the presence of calcium silicate with the aid of acetoacetic acid ethyl ester. A mixture of acetoacetic acid ethyl ester and isobutyl alcohol is a good solvent for calcium hydroxide, but does not dissolve calcium silicate. As solvent, use a mixture of 3 ml. of acetoacetic acid ethyl ester and 20 ml. of isobutyl alcohol; and to dissolve the calcium hydroxide, reflux the material to be analyzed with this solvent.⁵

Determination of copper. Interference by iron with the electrolytic determination of copper may be eliminated by the addition of acetoacetic acid ethyl ester.⁶

1. J. B. Cohen, *Practical Organic Chemistry*, 3rd ed., p. 98, Macmillan, London (1937).
2. J. Wislicenus, *Ann.* **186**, 161 (1877).
3. F. Feigl and E. Bäcker, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).
4. F. Feigl, *Qualitative Analyse mit Hilfe von Tüpfel Reaktionen*, 2nd ed. Akademische Verlagsgesellschaft, Leipzig (1935).
5. B. Franke, *Z. anorg. allgem. Chem.* **247**, 180-4 (1941); *C.A.* **36**, 5729 (1942).
6. Zen-Heo Pan, *Nanking J.* **2**, 193-9 (1932); *C.A.* **29**, 6528 (1935).

ACETONE

Synonym: Dimethylketone, propanone

 C_3H_6O

Mol. Wt. 58.08

Beil. Ref. I, 635(335).



Use: Detection of bismuth, chloride, cobalt, iron, mercury, molybdenum, nitrate, oxygen, selenium and thiocyanate.

Determination of barium, bismuth, calcium, chlorine, cobalt, copper, iodine, iron, molybdenum, potassium, selenate, selenium, strontium, sulfate, sulfur, thallium and thiocyanate.

Acetone is a colorless, clear, volatile, highly inflammable liquid. It possesses a characteristic odor and a pungent sweetish taste. It boils at 56.5° C. and has a sp. gr. of 0.788. It is miscible with water, alcohol, chloroform and ether. Commercial acetone contains from 0.1 to 0.5 per cent water.

Separation of calcium and strontium. Strontium may be separated from calcium by taking advantage of the fact that anhydrous calcium nitrate is quite soluble in acetone while strontium nitrate is practically insoluble. At room temperature 0.46 g. of calcium nitrate dissolves in 1 ml. of acetone in 1 hour and 45 minutes, while only 1.6 mg. of strontium nitrate dissolves under the same conditions.¹ The following procedure may be used for separating calcium and strontium:

Procedure. Precipitate strontium and calcium as the carbonates, wash the carbonate precipitate with water, and dissolve in nitric acid. Evaporate the resulting solution to dryness, and dissolve the calcium salt by treating the mixture with acetone.

Shreve, Watkins and Browning² have studied this separation and report that with 0.01 M solutions of strontium chloride, calcium chloride and calcium sulfate, at least 99.7 per cent of the strontium is recovered. Tillu and Telang,³ on the other hand, report that only fairly good results are obtained by evaporating a nitric acid solution containing calcium and strontium to dryness; and, after drying at 170° C., extracting the calcium nitrate with acetone.

Bailar⁴ has separated calcium and strontium by converting to the *p*-bromobenzoates and extracting the calcium salt in an acetone-water mixture. The alkali and ammonium bromobenzoates dissolve only to the extent of about 1 per cent in acetone containing 6 per cent water. The separation may be carried out as follows:

Procedure. Add 15 ml. of a saturated solution of ammonium *p*-bromobenzoate in 94 per cent acetone to 1 ml. of a solution containing strontium and calcium ions. The strontium is precipitated by this reaction whereas calcium remains in solution.

In general this method is not to be recommended, since many factors appear to affect the completeness of the separation. Separately a solution of strontium nitrate containing 1 mg. of the salt per ml. gives a distinct precipitate

with the above procedure, whereas a solution of calcium nitrate containing 50 mg. of the salt per ml. remains perfectly clear. Unfortunately, however, the solubility of the strontium salt is remarkably increased by the presence of other metallic salts, including calcium. If the concentration of calcium nitrate is only 3 or 4 times that of the strontium nitrate, precipitation does not occur at all. Bailar has studied the solubility of the *p*-chloro-, *p*-bromo-, and *p*-iodobenzoates in 94 per cent acetone. His results are given in Table 62.

TABLE 62.—SOLUBILITY OF CALCIUM, STRONTIUM AND BARIUM SALTS IN 94 PER CENT ACETONE EXPRESSED IN MILLIMOLES PER 100 ML.

	Calcium	Strontium	Barium
<i>p</i> -Chlorobenzoate	2.9	0.1	0.007
<i>p</i> -Bromobenzoate	1.79	820'0	Less than 0.003
<i>p</i> -Iodobenzoate	0.16	0.026	Less than 0.003

McElroy and Biglow⁵ have based a separation of calcium and strontium upon the fact that strontium chromate is soluble in 50 per cent acetone, while the corresponding strontium salt is insoluble. The following procedure may be employed:

Procedure. Dissolve the mixture of calcium and strontium carbonates in hydrochloric acid and evaporate to dryness on a water bath. Dissolve the residue in 50 per cent aqueous acetone, and treat with a solution of potassium chromate in 50 per cent acetone. Make alkaline with a drop of ammonia. Anhydrous strontium chromate begins to separate, and in about 10 minutes precipitation is complete. The calcium salt is not precipitated.

Williams and Briscoe⁶ have used acetone in the analysis of the alkaline earth metals. They have used this reagent in the precipitation of calcium, strontium, barium and magnesium as the carbonates. Strontium is precipitated as the chromate by means of acetone after the removal of barium as barium chromate, and calcium and strontium are then separated by means of acetone and *p*-toluic acid. Acetone is also used for the separation of calcium nitrate from the nitrates of barium and strontium.

Briscoe and Welcher⁷ and Duschak and Sneed⁸ have used an acetone-water mixture as the solvent for separating groups of anions in a systematic scheme of analysis. A rather general procedure for analyzing the anions consists in classifying the various ions according to the solubility of their barium, calcium, silver, zinc and other metallic salts. Barium chloride precipitates phosphate, sulfite, chromate, sulfate, and carbonate completely, but only incompletely precipitates arsenate, fluoride and oxalate from an aqueous solution. Calcium chloride completely precipitates oxalate and fluoride, but does not precipitate any other anions except those completely precipitated by barium. By using a mixture of barium and calcium chlorides, only arsenate, of the anions mentioned above, is incompletely precipitated.

With more concentrated solutions of the anions, a mixture of calcium and barium chlorides may also precipitate borate, thiosulfate, arsenite and tartrate. By adding 2 volumes of acetone to 1 volume of the aqueous solution containing the anions before precipitating with calcium and barium, a complete separation of borate, thiosulfate, arsenite, arsenate, and tartrate occurs. In addition, the ferrocyanide ion is also completely precipitated.

Separation of lithium from the alkali and alkaline earth metals. Lithium chloride may be quantitatively extracted with acetone from a mixture of the chlorides of lithium, sodium, potassium, barium and strontium, and finally determined by weighing as lithium sulfate. If sodium, potassium, barium and strontium are present in considerable quantity, two or more extractions may be necessary.⁴⁷

Lithium may be separated from rubidium, cesium and magnesium by this treatment, but the chlorides of the latter metals are slightly soluble in acetone, and a correction factor must be used to obtain fairly satisfactory results. Calcium must be absent in these separations.⁹

Detection and determination of the halogens. By treatment with potassium bromate, at a suitable acidity and in the presence of acetone, bromides and iodides are converted into non-ionizable bromoacetone and iodoacetone. In this way bromides and iodides may be eliminated as interfering substances in the detection and determination of chlorides with silver nitrate. Berg¹⁰ has used this reaction for the detection and determination of chlorine in the presence of bromine and iodine.

Procedure. To 50-60 ml. of the neutral halide solution add 20-30 ml. of acetone, sufficient sulfuric acid to make the solution 1-1.5 N at the end of the reaction, and a slight excess of 0.84 per cent potassium bromate solution. About 3-5 ml. of potassium bromate in excess is advisable. Immediately add 50 ml. of 5 per cent ferrous sulfate solution to destroy the excess bromate, and titrate the chloride with silver nitrate in the usual manner, adding sufficient 2 N nitric acid and ferric alum as the indicator.

Montequi and Puncel¹¹ have suggested an improvement of the method of Berg for detecting chlorides in the presence of bromides: the original method is tedious and the drop by drop addition causes some error.

Procedure. Add exactly 5 ml. of the solution to be analyzed to a 10-ml. graduated cylinder, and add 2 ml. of 20 per cent sulfuric acid and 3 ml. of acetone. Pour the mixture into a 50-ml. Erlenmeyer flask and heat to boiling. Remove from the flame and add dropwise, with shaking, a 5 per cent solution of potassium bromate in 2.5 N sulfuric acid. Each drop causes a yellow color, which disappears on shaking. When a slight color persists, add cold distilled water until the total volume is 30-40 ml., and add 8-10 drops of concentrated nitric acid, 2-3 drops of silver nitrate solution and shake. In the presence of chloride a turbidity appears in the mixture. An approximate idea of the quantity of the chloride can be obtained by adding more silver nitrate to observe the volume of precipitate produced.

In the presence of acetone, hydrogen iodide reacts with iodic acid according to the following equation:



Under proper conditions, this reaction takes place quantitatively without the oxidation of any bromide and chloride. Since the iodoacetone does not react with silver nitrate, bromides and chlorides may be detected or determined when mixed with iodides.¹²

Lewis¹³ has used a method for the determination of iodide with ceric sulfate which is based upon Berg's procedure for the elimination of iodine by the acid-catalyzed iodination of acetone.¹⁰

Procedure. A measured volume of the iodine solution is mixed with 25 ml. of acetone, 10 ml. of 9 N sulfuric acid and sufficient water to make the total volume 100 ml. Then add 1 drop of *o*-phenanthroline-ferrous sulfate solution, and titrate with ceric sulfate until the pink color of the indicator changes to blue.

Kolthoff, Laitinen and Lingane¹⁶ have studied this method and have reported the results as unsatisfactory. Lewis originally reported that with solutions 0.9-2.7 N in sulfuric acid the method gave results which were accurate to 0.1 per cent; below this range, low results were obtained, while above, results were high. According to Lewis¹⁵ the low results obtained by Kolthoff and his co-workers were obtained in solutions in which the initial concentration of sulfuric acid was 0.9 N. Since the reaction between acetone and iodine is acid catalyzed, the low results have been attributed to a low reaction rate. Since the end point of this reaction seldom lasts more than 3 minutes under the best conditions of acidity, it is probable that not a low reaction rate, but rather the production of new reducing substances which causes too much of the oxidant to be used is responsible for the error. The most suitable acidity appears to vary with the character of the oxidizing agent. Lewis was able to check ceric sulfate standardizations by the acetone method using potassium iodide with standardizations using sodium oxalate to within ± 0.1 -0.2 per cent.

Detection and determination of cobalt and thiocyanate. Cobalt and thiocyanate are often detected by means of the well-known Vogel reaction in which the blue color of the cobaltthiocyanate ion, $\text{Co}(\text{SCN})_4^-$, is detected by extracting in an amyl alcohol-ether mixture. This reaction may be made much more sensitive by substituting acetone for the amyl alcohol-ether mixture.¹⁷⁻²⁰

In a medium containing sufficient acetone or ethyl alcohol, an alkali thiocyanate produces a blue color with cobalt salts. This is due to the formation of a complex thiocyanate, probably $\text{Co}(\text{SCN})_4^-$. In an aqueous solution this complex is dissociated, and no color is formed unless a high concentration of thiocyanate is present. Acetone is preferred to ethyl alcohol for color formation, since a lower concentration is required. According to Tomula²⁴ the color reaches a practically constant maximum in a medium containing 50 per cent by volume acetone and a final concentration of 5 per cent ammonium thiocyanate. The sensitivity of this reaction in the presence of a little iron is much less than for cobalt alone regardless of the method used for the preliminary separa-

tion of iron.²¹ Kolthoff²² has used a 40-50 per cent acetone-alkali thiocyanate solution as a sensitive reagent for cobalt. Ferric ions, with which the thiocyanate forms a red color, may be made harmless by the addition of a soluble fluoride, but copper interferes and must be removed before making the test.

Cobalt may be detected by the blue color which is formed when ammonium thioacetate and stannous chloride are added to a solution of a cobalt salt²³ (see section on thioacetic acid). The reaction is made more sensitive by the addition of acetone, which reduces dissociation and extracts the color of the undissociated cobalt salt. Amyl alcohol appears to be more satisfactory for this purpose.

Thiocyanates may be detected by adding a drop of a solution of a cobalt salt and extracting the resulting compound with acetone.

Procedure. Evaporate a small quantity of the solution to be tested for thiocyanate to dryness, moisten with a drop of a solution of cobalt sulfate, and add 1 or 2 drops of acetone. This is a very delicate test for thiocyanates.

Tomula²⁴ has determined cobalt colorimetrically by converting to the colored $[\text{Co}(\text{CNS})_4]^-$ with ammonium thiocyanate, and comparing the resulting color with that of standards similarly prepared. The cobalt compound is dissolved in acetone rather than in methyl alcohol, ethyl alcohol or ether, since in acetone solutions the color is much stronger. The following procedure is used:

Procedure. Place 40 ml. of a neutral solution containing cobalt in a 100-ml. measuring flask and add 5 g. of ammonium thiocyanate and 50 ml. of acetone. Mix well and dilute to the mark, and compare the resulting color with that of standard solutions of cobalt which are similarly treated.

If small amounts of ferric iron and copper are present, add sufficient hydrochloric acid to make the acidity about 2 N and then add 3 ml. of a solution of 20 g. stannous chloride dihydrate in 100 ml. of 2 N hydrochloric acid for each 10 ml. of sample. Add ammonium thiocyanate and acetone as above and compare with a standard containing the same quantity of acid and stannous chloride as the unknown. When small quantities of nickel are present, use a yellow or yellow-green filter.

Results obtained by this method are shown in Table 63.

TABLE 63.—DETERMINATION OF COBALT BY THE THIOCYANATE METHOD IN AN ACETONE MEDIUM

Cobalt Used γ	Cobalt Found γ	Foreign Metals Present
34	35	
70	70	
340	350	
35	33	Nickel 35 γ
35	39	Nickel 117 γ
70	93	Nickel 210 γ
350	330	Nickel 350 γ
12	11.3	Nickel 125 γ

Mader²⁶ and Stengel²⁷ have used the cobalt-thiocyanate reaction for the determination of cobalt in plain and alloy steels. According to Mader, amyl alcohol is preferred to acetone for concentrations of cobalt ranging from 0.005 to 2.0 per cent, while acetone gives more satisfactory results for higher concentrations of cobalt ranging from 0.3 to 20 per cent.

Detection and determination of potassium. Potassium may be determined indirectly by precipitating as the cobaltinitrite with sodium cobaltinitrite, and, after dissolving the precipitate in nitric acid, determining the cobalt colorimetrically by means of ammonium thiocyanate in the presence of acetone.

Uhl²⁸ and Zinzadze²⁹ have used this procedure for the determination of potassium in biological material. The following procedure is described by Uhl²⁸:

Procedure. Ignite 5 g. of the material to be analyzed at a low temperature and dissolve the ash in 6 N hydrochloric acid. Dilute to 250 ml., precipitate with sodium carbonate and filter. Place 2 ml. of the filtrate in a calibrated 10-ml. centrifuge tube, neutralize with 0.1 N hydrochloric acid, add 2 ml. of 50 per cent sodium nitrite solution, 1 ml. of 25 per cent cobalt nitrate solution, and 1 ml. of a buffer solution prepared by mixing 40 ml. of saturated sodium acetate with 10 ml. of glacial acetic acid. Stir the mixture and allow to stand for 15 minutes, and then centrifuge for 5 minutes at 2000-3000 r.p.m. Draw off the supernatant liquid with the aid of a pipette and wash the precipitate 3 times with 4-ml. portions of a solution prepared by dissolving 10 g. of sodium acetate and 100 ml. of glacial acetic acid in a liter of distilled water. Dissolve the residue in 0.5 ml. of 6 N hydrochloric acid on a water bath, and boil for a time to remove the oxides of nitrogen. Add 1 ml. of a freshly saturated solution of sodium pyrophosphate and 1 ml. of a 60 per cent ammonium thiocyanate solution. Dilute with water to 5 ml., and then with acetone to 10 ml. The color is stable and may be compared in a colorimeter, or its extinction determined with a 600 or 620 m μ filter.

By means of the above procedure, which requires about 3 hours, as little as 12 γ of K₂O may be detected, and 0.5 mg. of potassium may be determined with a maximum error of 3.8 per cent.

Potassium is also determined volumetrically after precipitating as the potassium salt of dipicrylamine. In certain titration procedures based upon this reaction,^{30,31} the potassium salt of dipicrylamine is dissolved in acetone before the final titration. For the details of this procedure, see the section on dipicrylamine.

Detection and determination of molybdenum. In an acid solution, and in the presence of a suitable reducing agent such as stannous chloride, thiocyanates react with molybdenum to give an amber to orange-red color. This reaction may be used for the detection and colorimetric determination of molybdenum. Grimaldi and Wells⁵² recommend developing the color in an acetone-water mixture.

Detection and determination of iron. Iron may be detected and determined colorimetrically by means of the red color which is obtained when solutions of ferric salts are treated with soluble thiocyanates. The addition of a

miscible organic liquid having a low dielectric constant has been found to intensify the iron thiocyanate color. Acetone has been recommended for this purpose.^{32-34,54} In 60 per cent acetone solution the color is reported to be twice as strong as in an aqueous solution. Further, it has been shown that there is less interference from such substances as fluorides and oxalates in a water-acetone mixture than in water alone. For example, if the error is not to exceed 2 per cent, oxalate must be absent and not more than 30 p.p.m. of fluoride may be present when an aqueous solution is used. In a 60 per cent acetone-water solution, however, the determination can be carried out with the same accuracy when 400 p.p.m. of fluoride and 30 p.p.m. of oxalate are present.⁵⁴ The rate of fading of the iron thiocyanate color is lower when acetone is used than when water alone is the solvent. The general use of acetone to intensify the color of the iron thiocyanate reaction is somewhat restricted owing to the slight solubility of many salts in acetone-water mixtures.

The use of acetone in the iron determination is illustrated by the following procedure for the determination of iron in blood. This is taken from the work of Fowweather:³⁴

Procedure. Measure 1 ml. of blood into a test tube containing 4 ml. of distilled water and mix thoroughly. Transfer 1 ml. of this mixture to a 25 × 200 mm. test tube and add 1 ml. of concentrated sulfuric acid. Clamp the tube at an angle of 40° to the horizontal, and boil vigorously until all water has been expelled and white fumes appear. Remove the heat and allow the mixture to stand for 30 seconds, and then add dropwise 0.5 ml. of 30 per cent hydrogen peroxide. Again boil until white fumes appear and allow to cool for 30 seconds. Add an additional 0.5 ml. of peroxide as before, again heat, and if the solution does not become colorless add 0.3 ml. of peroxide. Continue heating for 1 minute after the solution becomes colorless. Allow to cool to room temperature and dilute with about 5 ml. of distilled water, and transfer to a 50-ml. stoppered graduated flask. Dilute to about 18 ml. and add 25 ml. of acetone. Mix thoroughly and allow to cool to room temperature. Finally add 5 ml. of 3 M ammonium thiocyanate, mix, and dilute to the mark. Simultaneously, prepare a standard solution as follows: place 1 ml. of standard iron solution containing 0.1 mg. iron per ml., and 1 ml. of concentrated sulfuric acid in a 50-ml. graduated flask. Dilute to 18 ml., add 25 ml. of acetone, mix, cool, add 5 ml. of 3 M ammonium thiocyanate and dilute to the mark. Compare the unknown and standard in a colorimeter.

If the standard is set at 20 mm., then

$$\frac{20}{R} \times 50 = \text{mg. iron per 100 ml. of blood, or}$$

$$\frac{20 \times 50}{R \times 3.35} = \text{hemoglobin in blood}$$

where R is the colorimeter reading of the unknown solution.

Detection of oxygen. Damon and Daniels³⁵ have observed that the photolysis of acetone is accompanied by a relatively intense green fluorescence,

but in the presence of a little oxygen a blue fluorescence is observed. This change of color has been used for detecting traces of oxygen in other gases.³⁶ The accuracy of this method is not great, but quantities of oxygen much smaller than can be detected by the usual tests may be detected.

Detection and determination of bismuth. Actone is used in the following test for bismuth, which has been proposed by Powell.³⁷

Procedure. To 10 ml. of an aqueous solution to be tested, add 2 ml. of dilute hydrochloric acid and 0.5 g. of potassium iodide. Mix well and add 5 ml. of acetone and 5-10 ml. of ethyl acetate and allow the layers to separate. A red color in the upper layer indicates the presence of bismuth.

Laporte⁴⁸ has used acetone to prevent the precipitation of the iodobismuthate in the colorimetric determination of bismuth as quinine iodobismuthate (see section on quinine).

Bismuth may also be determined colorimetrically by the formation of the orange double iodide with 8-hydroxyquinoline and extracting with a mixture of acetone and amyl alcohol.⁵³

Detection and determination of selenium. Selenium may be determined by converting to free selenium by means of suitable reducing agents. Hovorka³⁸ has used a solution of sulfur dioxide in acetone as a suitable reagent for the gravimetric determination of selenium.

Procedure. To 50 ml. of a solution containing 0.003-0.6 g. of selenium, add 5-20 ml. of a cold saturated solution of sulfur dioxide in acetone and heat gently. When the deposited selenium has become black and the supernatant liquid is clear, dilute with water and boil for 1 hour. Filter, wash, and weigh the selenium in the usual manner.

Low results are obtained with this method if the solution is made acid with sulfuric or tartaric acid, but good results are obtained when hydrochloric acid is used. Results are satisfactory with quantities of hydrochloric acid ranging from 5 ml. of N acid to 20 ml. of the concentrated acid.

Recently Ripan³⁹ has used acetone as a solvent in a method for the detection of selenic acid and for the separation of sulfates and selenates. This depends upon the fact that silver selenate is much less soluble than silver sulfate in solutions of pH 6.7. As little as 0.001 mg. of sodium selenate gives a precipitate with silver nitrate, and 0.0001 mg. of sodium selenate gives a precipitate of silver selenate in the presence of sodium acetate and acetone.

To separate sulfates and selenates proceed as follows:

Procedure. Dilute the solution until the concentration does not exceed 0.5 M, and add 4-6 drops of 2 N sodium acetate in 20 per cent acetone. Add 0.1 N silver nitrate with constant stirring. Filter off the precipitate of silver selenate and wash with acetone.

Acetone reaction with mercuric chloride. Deniges⁴⁰ reports that acetone yields a precipitate with an acid solution of mercuric chloride. This is probably due to enolization of the acetone.

Detection of nitrate. Acetone is used in a sensitive test for nitrates.⁴¹

Procedure. Add 12 drops of concentrated sulfuric acid and 2 drops of benzene to a crystal of solid nitrate and heat on a steam bath for 3 minutes. Then add 5-8 ml. of acetone and 3 ml. of 5 N sodium hydroxide solution. When the sodium hydroxide is added in excess an intense violet color appears, and this very slowly changes to violet, then red, and finally to a blood-red color.

Nitrobenzene may be used in place of benzene.

Miscellaneous uses. Acetone enjoys a rather wide variety of miscellaneous uses in analytical chemistry.

(a) Acetone is widely used as a solvent in many analytical procedures. A number of these have been discussed in the preceding sections. In addition to these, acetone is also widely used as a solvent for reagents such as dimethylglyoxime. It has also been used by Gapchenko⁴² as a solvent for cobalt α -nitroso- β -naphthol, and iron cupferron precipitates in indirect iron and cobalt determinations by titration methods.

(b) Acetone is also used as a wash liquid in analytical procedures. For example, Mach and Lepper⁴³ have used acetone to wash thallium chromate in the gravimetric determination of thallium; and Hevesey and Hobbie⁴⁴ have used acetone to dehydrate precipitates by repeated extractions.

(c) Castiglioni⁴⁵ has used acetone to extract sulfur from rubber for the determination of the sulfur.

(d) By passing dry hydrogen sulfide into pure acetone until the solution is saturated, a solution containing 22.4 g. of hydrogen sulfide per liter is obtained. This solution is stable for 6 to 12 months, and the hydrogen sulfide is not readily lost by exposure to air. After standing for about 1 year, thioketones are formed which are insoluble in water. The acetone solution of hydrogen sulfide can be used with considerable advantage in place of aqueous solutions of hydrogen sulfide in many analytical procedures requiring hydrogen sulfide as a reagent.⁴⁶

(e) The ionization constant of acetic acid in aqueous solution is $10^{-4.75}$ but in 75 per cent acetone it is $10^{-6.88}$, and in 50 per cent acetone it is $10^{-5.92}$; hence, solutions in these solvents can be titrated with 0.5-0.1 N aqueous hydrochloric acid with greater precision than is possible in aqueous solutions.²⁵

(f) Acetone is used in the indirect titration of sulfate with barium chloride, using sodium rhodizonate as the indicator.^{49,50}

(g) Interference by iron with the electrolytic determination of copper is eliminated by the addition of acetone.⁵¹

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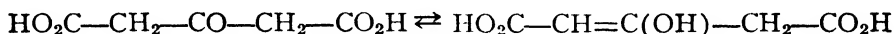
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ACETONEDICARBOXYLIC ACIDSynonym: β -Ketoglutaric acid

Mol. Wt. 146.10

Beil. Ref. III, 789.

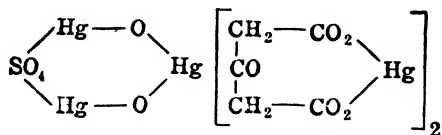
**Use:** Reactions with copper, iron, mercury and manganese.

This reagent is obtained as needles from acetic acid. It melts at 135° C. with decomposition. It is easily soluble in water and alcohol, but is less soluble in acetic acid, and only slightly soluble in ether. It is insoluble in chloroform and benzene.

Preparation: Add rapidly and with constant stirring 200 g. of finely powdered citric acid to 400 g. of fuming sulfuric acid (15 per cent SO_3) contained in a 2-liter flask. Carry out the reaction under a hood or in a well-ventilated place since carbon monoxide is evolved. When the reaction subsides, cool in a freezing mixture, and gradually add crushed ice to the flask. When thoroughly cooled, the mixture crystallizes to a thick paste. Filter through asbestos or glass wool, drain well, and dry on a porous plate. Purify by crystallization from ether.¹

Reaction with copper, iron, manganese and mercury. An aqueous solution of the reagent gives a light green crystalline salt with cupric acetate. It also reacts with ferrous ammonium sulfate to give a rose color, and with manganous chloride in the presence of ammonia to form a precipitate of reddish-yellow needles.²

Deniges³ reports that acetonedicarboxylic acid reacts with mercuric sulfate to form a compound of the following composition



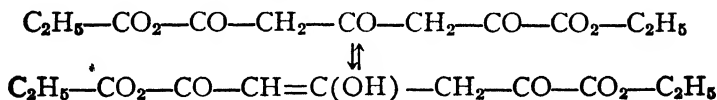
This compound is insoluble in water, but is soluble in hydrochloric acid.

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ACETONEDIOXALIC ACID ETHYL ESTER $C_{11}H_{14}O_7$

Mol. Wt. 258.22

Beil. Ref. III, 860(296).

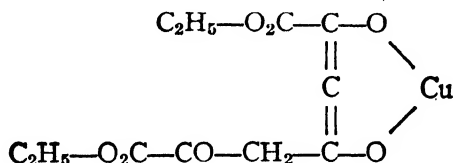
**Use:** Determination of copper.**Separation of copper from zinc and cadmium.**

The reagent is obtained principally as the monoenol form. This is a pale, yellowish-white, crystalline solid, melting at $104^\circ C$. It dissolves in 95 per cent alcohol to the extent of 1.5, per cent. It is difficultly soluble in water, but the alcoholic solution is not clouded by the addition of water.

Preparation: Dissolve 23 g. of sodium in 253 g. of absolute alcohol, and divide the resulting solution into two parts. Cool one half of the solution with ice water and pour in, with rotation, a moderately thick stream of a mixture of 29 g. of acetone and 73 g. of ethyl oxalate. Continue to rotate until the mass solidifies. Break up the mass with a stirring rod, and immediately pour in an additional 87 g. of ethyl oxalate. Equip the flask with an air condenser, and heat over a free luminous flame. When the sodium salt is dissolved, add the second portion of the ethylate. Swirl the mixture, and place the open flask in an oil bath at $110^\circ C$. When the mass has solidified, close the flask with a calcium chloride tube and allow to cool. Finally mix with 730 g. of 10 per cent hydrochloric acid in a mortar and stir thoroughly. Filter with suction, and wash with very dilute hydrochloric acid. Repeat the grinding, washing, and filtering.¹

Determination of copper and its separation from zinc and cadmium.

Copper is precipitated quantitatively when an alcoholic solution of the reagent is added to a solution of a copper salt. The precipitate does not occlude zinc or cadmium. It may be dried at $105^\circ C$. or ignited to CuO . The dried precipitate contains 19.88 per cent of copper, corresponding to the theoretical amount calculated for the formula $Cu(C_{11}H_{12}O_7)$.² The compound is probably the copper salt of the dienol form of the reagent.

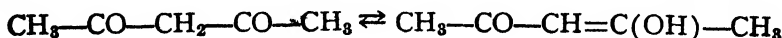
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Synonym: Diacetylmethane

 $C_5H_8O_2$

Mol. Wt. 100.11

Beil. Ref. I, 777.



Use: Detection of carbon disulfide, chromium, cobalt, hafnium, iron, manganese, thallium and zirconium.

Determination of fluoride and iron.

Acetylacetone is a colorless or slightly yellow, inflammable liquid. It possesses a very pleasant odor. It boils at 133-135° C. and has a sp. gr. of 0.976. It is soluble in about 8 parts of water, and is miscible with alcohol, chloroform, ether, benzene, acetone and glacial acetic acid.

Preparation: Press 25 g. of sodium wire into a 1.5-liter flask containing about 20 ml. of dry ether, and fit the flask with a reflux condenser and cool in a freezing mixture. Similarly cool 225 ml. of pure, alcohol-free ethyl acetate, and add to the flask containing the sodium. Then add in small portions 79 ml. of acetone which has also been cooled in a freezing mixture. Shake the flask constantly during the mixing. Take care that the acetone is not added too quickly because of the violence of the reaction; and not too slowly, since under these conditions a considerable quantity of ethylacetoacetate may be formed. After adding the acetone, allow the flask to remain for several hours in a freezing mixture, and then allow to stand for an additional 12 hours at room temperature. Dissolve the sodium salt of acetylacetone by adding 350-400 ml. of ice water, and separate the aqueous layer from the upper layer of ethyl acetate. Acidify the aqueous solution slowly with acetic acid. Boil 125 g. of finely powdered copper acetate with 1500 ml. of water for several hours, and filter off the undissolved basic salt. While this solution is still luke warm, add to the acidified solution containing acetylacetone to precipitate copper acetylacetone. Allow the precipitate to stand for several hours and filter, and then suspend the moist precipitate in ether. Add gradually, with shaking, dilute sulfuric acid until the solid disappears. Remove the lower layer of copper sulfate solution in a separatory funnel and dehydrate the upper ether layer with calcium chloride. Distill off the ether on a water bath, and fractionate the residue. Collect the portion boiling at 125-140° C. Purify by a second fractionation.^{1,2}

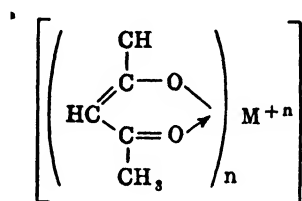
Acetylacetone may also be prepared from acetone and acetic anhydride in the presence of boron trifluoride.²¹

Preparation: Place 116 g. of dry acetone and 510 g. of reagent-grade acetic anhydride in a 2-liter, 3-necked flask and cool in an ice-salt mixture. Stopper one neck of the flask, fit the second neck with a tube for adding boron trifluoride and close the third neck with a stopper carrying an outlet leading to an alkali trap. Pass commercial boron trifluoride through a Kjeldahl bulb, and then bubble into the reaction mixture at such rate that 500 g. is absorbed in about 5 hours (about 2 bubbles per second). Pour the product into a solution of 800 g. of hydrated sodium acetate in 1600 ml. of water contained in a 5-liter flask. Distill with steam and collect the following portions: 1000 ml., 500 ml., 500 ml., and 400 ml.

Dissolve 240 g. of hydrated copper acetate in 3 liters of water by heating to 85° C. Filter, and precipitate the copper salt of acetylacetone by adding 1400 ml. of the hot filtrate to the first portion of the distillate from the steam

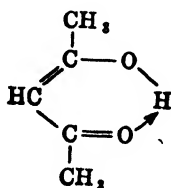
distillation; 700 ml. to the second; 500 ml. to the third; and 400 ml. to the fourth. Allow the mixture to stand 3 hours, or better overnight, in a refrigerator. Filter, wash once with water and suck as dry as possible. Shake the copper salt in a large separatory funnel with 800 ml. of 20 per cent sulfuric acid and 800 ml. of ether. Remove the ether layer, and again extract the aqueous layer with 400 ml. of ether and then with 200 ml. of ether. Combine the extracts and dry with 250 g. of anhydrous sodium sulfate. Remove the ether by distillation, and distill the acetylacetone through a fractionating column. Collect the fraction boiling at 134-136° C.

Metallic acetylacetonates. Acetylacetone, and other 1,3-diketones, form metallic compounds as a result of their ability to enolize. The acetylacetonates of practically all metals have been prepared,¹⁴ and most of these are inner-complex, non-electrolyte compounds



These compounds are exceptionally stable, and many can be distilled without decomposition at temperatures ranging over 300° C. They are also insoluble in water, but are soluble in polar solvents.

The acetylacetonates of boron, silicon and titanium have the following composition:^{15,16} $[(\text{Acac})_2\text{B}]\text{X}$; $[(\text{Acac})_3\text{Si}]\text{X}$ and $[(\text{Acac})_3\text{Ti}]\text{X}$, in which *Acac* represents the anion of acetylacetone. Sidgwick¹⁷ concluded from a study of the chemical and physical properties of acetylacetone that the enol form is essentially, if not completely, a cyclic structure in which the enolic hydrogen is coordinated to the carbonyl oxygen atom. This is further confirmed by the fact that the characteristic hydroxyl absorption in the infrared is not obtained with this compound.¹⁸ The cyclic structure is



Detection of thallium and carbon disulfide. Like other enolizable diketones, acetylacetone gives a characteristic reaction with thallium and carbon disulfide.³⁻⁵ Thallium acetylacetonate is prepared by boiling thallium carbonate with an alcoholic solution of the reagent. The pure product is obtained by filtration and crystallization from the filtrate. The thallium salt consists of small

white needles with a brownish shade. With carbon disulfide this compound reacts to give a voluminous orange colored precipitate (page 391). The thallium complex with carbon disulfide appears to be derived from the dienol form of acetylacetone, which is made stable through complex formation (page 13).

This reaction serves as a delicate test for carbon disulfide.

Procedure. Add 1 drop of carbon disulfide to an alcoholic or benzene solution of thallium acetylacetonate. A yellow precipitate or a yellowish turbidity appears with only traces of carbon disulfide, and with larger quantities of this compound an orange precipitate is formed.

Other organic compounds containing sulfur also give precipitates with thallium acetylacetonate, but these have colors differing from that with carbon disulfide.

Reactions with zirconium, and hafnium. Zirconium and hafnium form salts when treated with acetylacetone. The zirconium compound, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$, has been prepared by Biltz and Clinch⁶ by adding acetylacetone to a solution of $\text{ZrO}(\text{NO}_3)_2$. The hafnium compound, $\text{Hf}(\text{C}_5\text{H}_7\text{O}_2)_4$, has been prepared by Hevesey and Lögstrup⁷ as follows:

Procedure. Dissolve 10.1 g. of $\text{HfOCl}_2 \cdot 6\text{H}_2\text{O}$ in 65 ml. of water, and add 15 ml. of acetylacetone and 75 ml. of 10 per cent sodium carbonate solution.

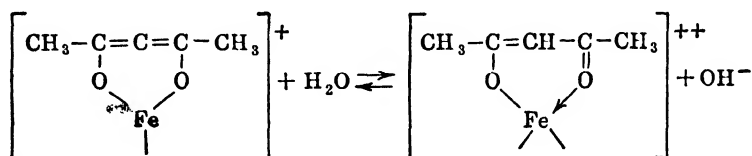
Both the zirconium and hafnium compounds are soluble in alcohol, carbon tetrachloride, and carbon disulfide. Solutions of these compounds in carbon disulfide give a characteristic red color. Thallium does not give this reaction.

Reactions with iron, manganese, chromium and cobalt. Urbain and Debiere⁸ have prepared the following metallic salts of acetylacetone: (a) The ferric compound is obtained as a red crystalline solid from benzene (m.p. = $184^\circ\text{C}.$); (b) the manganese salt is obtained as black glistening crystals from alcohol (m.p. = $172^\circ\text{C}.$); (c) the cobalt compound is obtained as black crystals or as a light green powder (m.p. = $240^\circ\text{C}.$); (d) the chromium compound is a reddish-violet crystalline solid (m.p. = $214^\circ\text{C}.$).

Reaction with manganese, calcium, zinc, cadmium and mercury. Tantar and Kurovskii⁹ have prepared a number of metallic derivatives of acetylacetone. Among these are the compounds of magnesium, calcium, zinc, cadmium and mercury.

Determination of iron. Combes⁵ first prepared acetylacetone and mentioned the red color which appears when it is treated with solutions containing ferric salts. Ferric acetylacetonate is prepared by shaking ferric hydroxide with an alcoholic solution of the reagent. Aqueous solutions of ferric acetylacetonate are non-conducting, and it is therefore assumed that this compound is a chelate salt. There is a tendency for this compound to undergo hydrolysis, and this must be controlled in the analysis of iron by a very low concentration of acid. Since the color of the iron is quite sensitive to variation in pH, this

factor must be rigidly controlled during the determination. The ferric compound is also decomposed by alkalis with the precipitation of ferric hydroxide,¹¹ and too much acid tends to weaken the color. It thus appears that the more highly colored form is that in which ring closure is affected by a coordination bond, rather than one in which both hydrogen atoms of the enolized form of the reagent have been replaced by the metal. This is represented by the following equilibrium.



These mono- and divalent ions may combine with other molecules of acetylacetone to form completely undissociated molecules.^{10,11}

Pulsifer¹² has used the reaction between ferric ions and acetylacetone as the basis for a very satisfactory method for the colorimetric determination of small quantities of iron. The following procedure may be employed to determine iron in the analysis of water:

Procedure. Evaporate 100 ml. of the water to be analyzed to dryness on a water bath, and remove the organic matter by treating with sulfuric and nitric acids. The iron oxide which is present in the ignited residue is dissolved by warming with a few drops of dilute sulfuric acid and a drop of hydrochloric acid.

If much insoluble residue remains, filter the mixture into a porcelain dish; and, after washing the filter, oxidize the iron with a few drops of hydrogen peroxide or nitric acid. If only traces of iron are present, evaporate the solution almost to dryness to expel the excess acid, and transfer the solution to a 50-ml. Nessler tube. Add 2 ml. of a 0.5 per cent aqueous or alcoholic solution of the reagent and dilute to the mark with distilled water. If larger quantities of iron are present, the small amount of acid need not be removed by evaporation, but the mixture should be diluted to 500 or 1000 ml. and an aliquot of this solution treated as described above. The contents of the tube should be well mixed, and the resulting color compared with standards similarly prepared. For accurate work, conditions of acidity, excess of reagent, and volume of standards and unknown must be the same.

The smallest amount of iron that can be detected by the above procedure is 0.003 mg., and the smallest quantity detectable with thiocyanate is 0.006 mg. Salicylic acid possesses a sensitivity as an iron reagent similar to that of the thiocyanate, but the color formed with this compound fades rapidly. Acetylacetone also possesses an advantage over thiocyanate in that the range of the iron concentration is somewhat greater. The largest amount of iron determinable by this method is about 0.6 mg. The iron test with acetylacetone may be used in all cases where potassium thiocyanate can be employed. Quantities of

sodium, potassium, calcium, strontium, barium, magnesium, zinc, lead, manganese, cadmium, aluminum, mercury, chloride, bromide, sulfate, citrate, chlorate, and arsenic lower than 0.2 g. have no effect upon this determination. Smaller amounts of silicic and phosphoric acid and of copper do not interfere. The oxides of nitrogen give a brown color with acetylacetone and ammonia gives a strong yellow color. In very dilute solutions most other ions do not interfere. Small changes in temperature are also without appreciable effect.

The color does not vary uniformly with variation in depth of liquid so that only the duplication method is suitable. The solubility of iron acetylacetonate is approximately 1.5 g. per liter.

In a recent critical study of reagents used for the determination of iron by Wenger and Duckert,²⁰ acetylacetone was recommended as one of the most satisfactory of all which have been studied.

Determination of fluorine. Soluble fluorides may be determined by their fading action upon the color of a solution of ferric acetylacetonate. The color of the unknown solution is compared directly with standards having the same acidity and containing the same foreign ions and in approximately the same proportions as the unknown. The color readings plotted against the fluoride content give a straight line instead of a hyperbola as required by Beer's law. The following procedure has been described by Armstrong.¹³

Reagent. Acetylacetone reagent: Use a 0.5 per cent aqueous solution of freshly distilled acetylacetone.

Ferric chloride solution: Prepare a solution of ferric chloride which contains 0.3 mg. of iron per ml. Protect this solution from light and discard after about 3 hours.

Standard fluoride solution: Prepare a solution of sodium fluoride of known purity so that 1 ml. contains 0.1 mg. of fluoride.

Procedure. If the solution to be analyzed contains carbonates, add a few drops of phenolphthalein, and add 0.1 N hydrochloric or nitric acid dropwise to the boiling solution until it no longer turns pink on further boiling. Immediately add 0.1 N sodium hydroxide solution until the mixture is slightly alkaline, and allow to cool in a stoppered flask. Make the above solution, or one not containing carbonates, just acid to phenolphthalein and add 1 drop of 1:100 acid.

To each of two 25-ml. volumetric flasks, transfer 1 ml. of the ferric chloride solution and 1 ml. of the reagent solution. To one of the flasks, add an aliquot of the unknown solution containing not more than 0.25 mg. of fluoride, and then dilute the mixtures in both flasks to the mark. Compare the solutions in a colorimeter with the solution containing no fluoride in the left cup with the colorimeter set at 20 mm. Take 20 readings by increasing the depth of the solution in the right cup and average the results. Repeat the procedure with the same size aliquot of the unknown solution, adding 1 ml. (0.1 mg. of fluoride) of the standard solution of sodium fluoride to the flask containing the unknown. Again take 20 readings as before and determine the average.

Calculate the results using the following equation:

$$F = \frac{(X - 20) \times D \times 0.1}{(y - x)}$$

F = fluorine content of the total solution in mg.

X = reading of the unknown.

Y = reading of the unknown + 1 mg. of fluorine.

D = ratio of the total volume of the solution to the volume of the aliquots.

This method has been found to be more accurate because it is less susceptible to the effect of sulfate and chloride than the ferric thiocyanate method, measurements being with a photoelectric cell.¹⁹ Quantities of sodium chloride and sodium sulfate as high as 0.1 g. and 0.2 g., respectively, alter the color of ferric acetylacetone, but 0.05 g. of sodium chloride and 0.1 g. of sodium sulfate, alone or together are without influence on the color.

The colorimeter should be used with a blue filter, since the colors of solutions containing different concentrations of ferric acetylacetone vary from red to yellow and consequently cannot be matched directly.

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3. F. Feigl and E. Bäcker, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).
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5. A. Combes, *Compt. rend.* **105**, 868 (1888).
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11. A. Hantzsch and C. H. Desch, *Ann.* **323**, 1 (1902).
12. H. B. Pulsifer, *J. Am. Chem. Soc.* **26**, 967 (1904).
13. W. D. Armstrong, *Ind. Eng. Chem., Anal. Ed.* **5**, 300-2 (1933); *C.A.* **27**, 5273 (1933).
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16. W. Dilthey, *J. prakt. Chem.* [2] **111**, 147 (1925).
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19. L. V. Wilcox, *Ind. Eng. Chem., Anal. Ed.* **6**, 167-9 (1934).
20. P. Wenger and R. Duckert, *Helv. Chim. Acta.* **27**, 757-70 (1944); *C.A.* **38**, 6228 (1944).
21. C. E. Denoon, Jr., *Organic Synthesis*, Vol. 20, p. 6.

ACETILPYRORACEMIC ACID ETHYL ESTER

Synonym: Acetoneoxalic ester, ethyl acetopyruvate

$C_7H_{10}O_4$

Mol. Wt. 158.15

Beil. Ref. III, 747(261).



Use: Reaction with thallium, copper, and ferric chloride.

Acetylpyrroacemic acid ethyl ester is a solid melting at 18° C., and boiling at 213-215° C.

Preparation: Place 280 ml. of absolute alcohol in a flask and slowly add 12.5 g. of sodium. Allow the mixture to cool to room temperature with stirring, and slowly add a mixture of 67 ml. of ethyl oxalate and 36.6 ml. of acetone. Continue stirring for a time after the addition of the ethyl oxalate-acetone mixture and filter the yellow sodium salt. Rinse the flask with 20 ml. of absolute alcohol, which is then used to wash the precipitate. Dry the precipitate with suction and return to the flask. Add 150 ml. of water and 100 g. of cracked ice. Stir and add rapidly a solution of sulfuric acid prepared by adding sufficient ice to 20 ml. of concentrated sulfuric acid so that some of the ice is not melted. Stir until the yellow sodium salt disappears. Extract the mixture with three 60-ml. portions of benzene. Remove the benzene from the extracts on a water bath, and distill the crude product under reduced pressure. The compound boils at 130-132° C. at 37 mm. pressure.^{1,2}

Reactions. Acetylpyrroacemic acid ethyl ester reacts with thallium salts to form a yellow derivative, but this does not react with carbon disulfide. Acetylpyrroacemic acid ethyl ester also forms a yellowish-green copper derivative, having the formula $\text{Cu}(\text{C}_7\text{H}_9\text{O}_4)_2$; and, like other enolic compounds, gives a deep red color with ferric chloride.³

1. L. Claisen and N. Stylos, *Ber.* 20, 2189 (1887).

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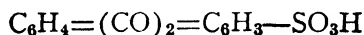
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ANTHRAQUINONE- β -SULFONIC ACID

$\text{C}_{14}\text{H}_8\text{O}_5\text{S} \cdot 3\text{H}_2\text{O}$

Mol. Wt. 342.31

Beil. Ref. XI, 337.



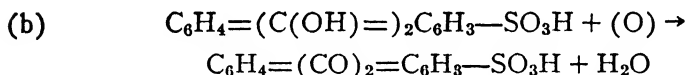
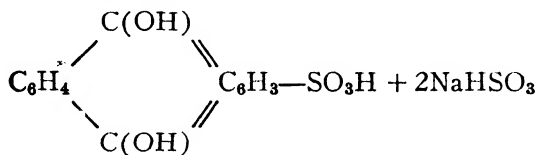
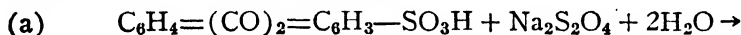
Use: Reagent for the absorption of oxygen.

The sodium salt of anthraquinone- β -sulfonic acid occurs as silvery leaves. It is very soluble in cold water. 100 ml. of hot saturated aqueous solution contains 21 g. of the salt, while 100 ml. of a cold solution contains only 0.83 g. of the salt.

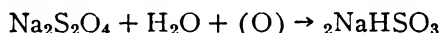
Preparation: Place 30 g. of fuming sulfuric acid (40 per cent SO_3) in a flask and add 30 g. of anthraquinone. Attach the flask to an air condenser, and heat the mixture in a paraffin or metal bath to 150-160° C. for 8 hours. Pour the mixture while hot into a large vessel containing about a liter of cold water, and boil for an hour. Filter with suction, replace the precipitate in the vessel, and boil again with 500 ml. of water. Again filter, and finally wash once or twice with boiling water. Combine the filtrate and washings, add 0.2 g. of potassium chlorate, and evaporate to approximately 500 ml. Nearly neutralize with sodium carbonate solution (about 120 g. of crystalline sodium carbonate). Do not completely neutralize as the sodium salt of the monosulfonic acid is less

soluble in presence of an acid. Evaporate on a water bath until a scum appears on the surface of the liquid, and then allow the mixture to cool. The sodium salt of the sulfonic acid crystallizes in pale yellow crystals, which are separated by suction. Wash 3 or 4 times with water that has been slightly acidified, and dry on a porous plate.¹

Absorption of oxygen. A mixture of sodium anthraquinone- β -sulfonic acid and sodium hydrosulfite, $\text{Na}_2\text{S}_2\text{O}_4$, in dilute alkali hydroxide solution absorbs oxygen rapidly. The action of the reagent is catalytic, and takes place according to the following equations:



The net result of these reactions is expressed in the following equation:

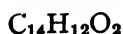


Under the best conditions obtainable, sodium anthraquinone- β -sulfonate is less rapid in its action than an alkaline pyrogallol solution. Consequently, pyrogallol would be more suitable as an absorbent for oxygen were it not for the fact that considerable difficulty is encountered in eliminating the error arising from the evolution of carbon monoxide during the oxidation of the reagent, and further that this viscous reagent is difficult to handle in certain types of apparatus.²

Kruse³ recommends a solution consisting of 15-20 per cent sodium hydrosulfite, 1-2 per cent sodium anthraquinone- β -sulfonate, and 10 per cent potassium hydroxide as the best mixture for the absorption of oxygen, although according to him this reagent is not as satisfactory as pyrogallol. Quiggle⁴ has studied the use of anthraquinone- β -sulfonic acid and recommends the mixture originally suggested by Fieser, which is prepared by dissolving 16 g. sodium hydrosulfite, 13.3 g. sodium hydroxide and 4 g. of sodium anthraquinone- β -sulfonate in 100 ml. of water.

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2. L. F. Fieser, *J. Am. Chem. Soc.* **46**, 2639-47 (1924); *C.A.* **19**, 449 (1925).
3. T. K. Kruse, *J. Pharmacol. Proc.* **25**, 151 (1925); *C.A.* **19**, 3232 (1925).
4. D. Quiggle, *Ind. Eng. Chem., Anal. Ed.* **8**, 363 (1936); *C.A.* **30**, 7480 (1936).

BENZOIN



Mol. Wt. 212.24 Beil. Ref. VIII, 166(572).



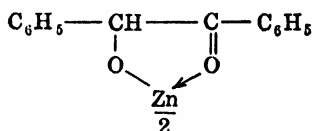
Use: Detection of zinc.

Benzoin is a white crystalline solid melting at 133-134° C. and boiling at 344° C. It is only very slightly soluble in cold water, but is more readily soluble in boiling water. It is soluble in acetone or boiling alcohol but is only slightly soluble in ether.

Preparation: Mix 25 g. of benzaldehyde, a solution of 5 g. of sodium or potassium cyanide in 20 ml. of water and 50 ml. of alcohol, and heat on a water bath under reflux for about one-half hour. Allow the mixture to cool and filter off the crystals of benzoin and wash with a little alcohol. The compound is purified by recrystallizing from ethyl alcohol.^{1,2}

Detection of zinc. White and Neustadt³ have used a fluorescent reaction of benzoin with zinc as a means of detecting very small quantities of the zinc ion. The fluorescence of zinc appears in an alkaline solution in the presence of magnesium hydroxide. The magnesium hydroxide adsorbs the fluorescent compound to increase the sensitivity of the test. The fluorescence can be made more lasting by addition of a small quantity of a silicate to the reaction mixture; in this case it is probable that the adsorbing agent is a basic magnesium silicate.

Since benzoin possesses a structure capable of forming chelate compounds with metals, it appears probable that zinc forms a compound of the following composition:



Reagents. *Sodium hydroxide-sodium silicate:* Mix 100 ml. of 2.5 N sodium hydroxide with 0.6 ml. of 35 per cent sodium silicate solution. The sodium silicate is unnecessary if immediate observations are to be made.

Sodium dithionite: Dissolve 1 g. of sodium dithionite in 25 ml. of water. This solution should be prepared the day it is used.

Benzoin reagent: Dissolve 0.3 g. of benzoin in hot 95 per cent ethyl alcohol.

Magnesium nitrate solution: Dissolve sufficient magnesium nitrate in water so that 1 liter of solution contains 2 g. of magnesium ion.

Procedure. Make the solution to be tested (containing at least 0.1 mg. of zinc ion), neutral or slightly alkaline with sodium hydroxide solution, and add sufficient sodium hydroxide to dissolve the precipitated zinc hydroxide. Any hydroxides which are insoluble in sodium hydroxide are removed by filtration. The volume of the solution should be between 5 and 15 ml. Add approximately 1 ml. of each of the above reagents in the order in which they are given. Shake well and after a minute or two observe under an ultraviolet lamp. A green fluorescence between 4650 and 5700Å. is a positive test. The G.E. H-4 lamp with a blue-purple bulb is the most satisfactory source of ultra violet light. If much visible light is present, the fluorescence should be observed through a piece of green cellophane. For concentrations of zinc less than 0.1 mg., a blank

should be run simultaneously. The fluorescence increases for the first few minutes after the solutions are mixed, and then it fades very slowly and finally disappears completely.

Both beryllium and boron give a fluorescence with benzoïn. The beryllium color lies in the yellow-green range from 4930 to 5700 Å., and that with boron from 4710 to 5700 Å. Both of these ions fluoresce before the addition of magnesium hydroxide, and if the mixture is examined under the ultraviolet lamp at this point they should not be confused with the zinc test. Zinc can be distinguished from beryllium after the addition of the magnesium hydroxide by comparing with a standard. Antimony also gives a purplish fluorescence that will completely mask the green color of zinc. The platinum metals, mercury, silver and gold also cause some difficulty since the ions of these elements are reduced to the metal by the dithionite which is used in the test. Anions of molybdenum, vanadium, tellurium, and selenium also cause interference due to reduction with the dithionite. Chromates, permanganates and iron cyanides interfere due to their color. The alcoholic solution of benzoïn has a faint greenish fluorescence, but upon dilution in the test this causes no interference. Sodium dithionite is added to prevent oxidation of the benzoïn.

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2. N. Zinin, *Ann.* 34, 186 (1840).
3. C. E. White and M. H. Neustadt, *Ind. Eng. Chem., Anal. Ed.* 15, 599-600 (1943); *C.A.* 37, 6582 (1943).

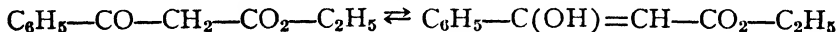
BENZOYL ACETIC ACID ETHYL ESTER

Synonym: Ethyl benzoyl acetate

$C_{11}H_{12}O_3$

Mol. Wt. 192.21

Beil. Ref. X, 674.



Use: Detection of carbon disulfide.

Benzoyl acetic acid ethyl ester is a liquid boiling at 270° C. with slight decomposition. It is volatile with steam. It is easily soluble in alcohol or ether, but is difficultly soluble in water.

Preparation: Place 136 g. of sodium ethoxide (for preparation, see reference¹ and 300 g. of ethyl benzoate in a 1-liter, 3-necked flask fitted with a mercury-seal stirrer, a dropping funnel extending below the surface of the liquid, and a reflux condenser carrying a calcium chloride tube at the upper end. Stir the mixture, and heat to 70-80° C. on an oil bath until a fairly homogeneous paste is formed. Then add slowly from the dropping funnel 176 g. of ethyl acetate. The addition of this compound should require about 2 hours. Raise the temperature of the oil bath to 90° C., and keep it at this temperature for 2 hours while the mixture is stirred. At the end of this time, cool the mixture, and add a cold solution of 150 ml. of glacial acetic acid in 300 ml.

of water. Shake the mixture with ether, wash the ether extract with sodium bicarbonate, remove the ether, and distill under reduced pressure.²⁻⁵

Detection of carbon disulfide. Benzoyl acetic acid ethyl ester does not form a thallium derivative, but an orange-red compound with thallium and carbon disulfide is formed. The composition of this compound is represented by the formula $C_{12}H_{10}O_3S_2Tl_2$.⁶

1. S. M. McElvain, *J. Am. Chem. Soc.* **51**, 3128 (1929).
2. R. L. Shriner and A. G. Schmidt, *J. Am. Chem. Soc.* **51**, 3636 (1929).
3. J. B. Dorsch and S. M. McElvain, *J. Am. Chem. Soc.* **54**, 2960 (1932).
4. R. E. Lutz and F. N. Wilder, *J. Chem. Soc.* **56**, 1989 (1934).
5. *Organic Synthesis* **18**, 33-35 (1938).
6. F. Feigl and E. Bäcker, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).

BENZOYL ACETONE

Synonym: methyl phenacyl ketone

$C_{10}H_{10}O_2$

Mol. Wt. 162.18

Beil. Ref. VII, 680.



Use: Detection of thallium.

Benzoylacetone is a crystalline solid having a penetrating and persistent odor. It melts at 57-58° C. It is difficultly soluble in water, but is easily soluble in alcohol and ether.

Preparation: Prepare sodium ethoxide as follows: Dissolve 4 g. of sodium in 40 ml. of absolute alcohol, and distill off the excess of alcohol, first from a water bath, and then from a metal bath in a current of dry hydrogen, and finally elevate the temperature of the mixture gradually to 200° C. until nothing further distills over. Quickly powder the white solid, weigh out 6 g., and add to 20 g. of ethyl acetate and cool the mixture in water. Allow to stand 15 minutes, and add 10 g. of acetophenone. Add a little ether and allow to stand for several hours. Filter the separated sodium compound, wash with ether, and dry in air. To obtain free benzoyl acetone dissolve the sodium compound in cold water and acidify with acetic acid.¹

Detection of thallium. Benzoyl acetone forms a light yellow derivative with thallium, but this does not react with carbon disulfide.²

1. J. B. Cohen, *Practical Organic Chemistry*, 3rd ed., p. 259, Macmillan, London (1937).
2. F. Feigl and E. Bäcker, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).

BENZOYLPYRORACEMIC ACID ETHYL ESTER

$C_{12}H_{12}O_4$

Mol. Wt. 220.22

Beil. Ref. X, 815(395).



Use: Detection of thallium.

This reagent is obtained as prisms by crystallizing from petroleum ether. It melts at 42° C. and is readily soluble in the common solvents.

Preparation: Dissolve 9.2 g. of sodium in 150 ml. of alcohol, cool to 0° C., and mix with 48 g. of acetophenone, and then with 58.4 g. of diethyl oxalate and shake vigorously. Allow the mixture to stand 12 hours. Stir the separated sodium salt with ether, filter with suction, and dry the solid on a porous plate. Dissolve in ice water, and decompose with carbon dioxide.¹

Detection of thallium. Benzoylpyrrolacemic acid reacts with thallium salts to yield a yellow thallium derivative, but unlike the thallium salts of other enolic compounds, this substance does not react with carbon disulfide.²

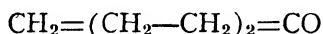
1. C. Beyer and L. Claisen, *Ber.* **20**, 2181 (1887).
2. F. Feigl and E. Bäcker, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).

CYCLOHEXANONE

C₆H₁₀O

Mol. Wt. 98.14

Beil. Ref. VII, 8.



Use: Determination of bismuth.

Cyclohexanone is a colorless, oily liquid which has a peppermint-like odor. Its sp. gr. is 0.948 and it boils at 155° C. It is soluble in water, alcohol and ether.

Preparation: Dissolve 42 g. of sodium dichromate in 200 ml. of water and add 19 ml. of concentrated sulfuric acid with stirring. Cool to 30° C. and add to 21 ml. of cyclohexanol contained in a 500-ml. Erlenmeyer flask. Shake the mixture and observe the temperature with the aid of a thermometer immersed in the liquid. When the temperature reaches 55° C., cool the flask so that the temperature does not rise above 60° C. nor fall below 55° C. When the temperature no longer rises above 60° C. upon the removal of external cooling, allow the mixture to stand for 1 hour with occasional shaking. Transfer the mixture to a 1-liter round-bottom flask and add 200 ml. of water and attach to a condenser. Heat the mixture and collect 100 ml. of distillate. Saturate the aqueous layer of the distillate with salt, separate the upper cyclohexanone layer and then extract the aqueous layer with 20 ml. of ether. Combine the ether extract and the cyclohexanone and dry with 5-6 g. of anhydrous magnesium sulfate. Transfer the dried solution to a distilling flask and remove the ether on a water bath. Then distill the cyclohexanone and collect the fraction boiling at 150-155° C.

Determination of bismuth. Small quantities of bismuth may be determined colorimetrically by comparing the color of a solution of quinine iodo-bismuthate in cyclohexanone with that of standards similarly prepared¹ (see section on quinine).

1. A. Okac, *Chem. Listy.* **32**, 27-30 (1938); *C.A.* **32**, 5326 (1938).

DIBENZOYLMETHANE

Synonym: Phenyl- α -hydroxystyryl ketone, β -hydroxychalkone

$C_{15}H_{12}O_2$

Mol. Wt. 224.25

Beil. Ref. VII, 769.



Use: Detection of carbon disulfide and thallium.

Dibenzoylmethane is a crystalline solid melting at 76-78° C. It dissolves readily in alcohol, ether and chloroform. It is insoluble in sodium carbonate but dissolves readily in sodium hydroxide.

Preparation: *Benzalacetophenone dibromide.* Dissolve 21 g. of benzalacetophenone in 60 ml. of carbon tetrachloride, cool in an ice bath, and add 26 ml. of bromine. When the reaction is complete, filter off the dibromide and wash with two 25-ml. portions of hot alcohol.

Dibenzoylmethane. Mix 18.4 g. of benzalacetophenone dibromide and 16.5 ml. of methyl alcohol and add rapidly a solution of sodium methylate previously prepared from 2.3 g. of sodium and 23 ml. of absolute methyl alcohol. Reflux the mixture for some time, and add sufficient hydrochloric acid to neutralize the mixture. Add an additional 0.4 ml. of hydrochloric acid, reflux for an additional 5 minutes and add 16 ml. of cold water. Cool the flask in ice water and filter. Wash with about 5 ml. of 50 per cent methyl alcohol and wash with water until free of acid. Purify by recrystallizing from a little hot methyl alcohol.¹

Reaction with thallium and carbon disulfide. By heating a solution of dibenzoylmethane in absolute xylene with thallium carbonate and filtering, a yellow crystalline compound having the composition $C_{15}H_{11}O_2Tl$ is obtained from the filtrate. By treating the xylene solution of the thallium compound in dry benzene with carbon disulfide a carmine red compound, $C_{16}H_{16}O_2S_2Tl$, is formed.

1. *Organic Synthesis*, Collective Vol. I, 2nd ed., p. 205, John Wiley, New York (1941).
2. F. Feigl and E. Backer, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).

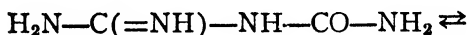
DICYANDIAMIDINE

(Synonym: Guanylurea, biuretamidine)

$C_2H_6ON_4$

Mol. Wt. 102.07

Beil. Ref. III, 89(42).



Use: Detection of cobalt, copper and nickel.

Determination of copper and nickel.

Dicyandiamidine sulfate is a white crystalline solid which crystallizes from water with 2 molecules of water of hydration. At 110° C. the anhydrous com-

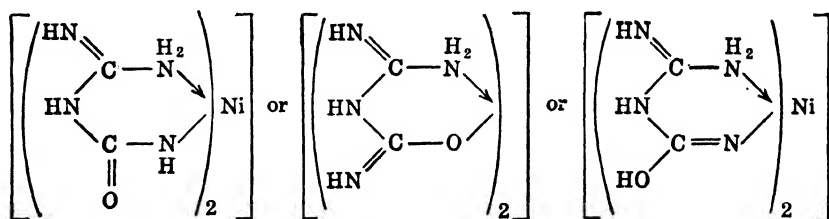
pound is formed. The reagent is soluble in about 20 parts of cold and 3 parts of boiling water and is slightly soluble in alcohol. It is insoluble in ether.

Preparation: Dilute concentrated sulfuric acid with an equal volume of water and add calcium cyanamide slowly with shaking. Extract the mass with water at 80-90° C. and concentrate the resulting solution by evaporation. Filter off the calcium sulfate which first precipitates, and then recover the dicyandiamidine sulfate which is obtained by further evaporation of the filtrate. Purify by recrystallizing from hot aqueous alcohol.

Dicyandiamidine may also be prepared from dicyandiamide by the following method:

Dilute 180 g. of concentrated sulfuric acid with 3 times as much water and add gradually to the hot liquid 300 g. of dicyandiamide. Dilute to 1500 ml., warm 10 minutes on a water bath, and cool with shaking to 40° C. Mix the suspension of the sulfate which forms with the calculated quantity of barium hydroxide (about 580 g.), shake, filter, and evaporate the solution in vacuum (10-12 m.m.), first at room temperature and finally at 40° C. The conversion of the sulfate to the free compound may be omitted if the sulfate is to be used as the reagent.¹

Detection of nickel. Dicyandiamidine reacts with nickel to form a yellow chelate salt which may be used for the detection and determination of nickel. It appears that a keto and enol form of the reagent are in equilibrium with one another. Upon the replacement of the labile hydrogen atom by a metal such as nickel, a 6-membered chelate ring is formed by coordination with one or both of the terminal nitrogen atoms. The following structure has been assigned to the nickel complex.^{2,3,20}



Grossmann and co-workers⁴⁻⁹ have suggested the use of dicyandiamidine as a very sensitive reagent for nickel, and its usefulness has been confirmed by the studies of Wenger and co-workers.¹⁰ A 5 per cent aqueous solution of dicyandiamidine in a strongly alkaline solution gives a yellow precipitate with as little as 10γ of nickel in a volume of 0.01 ml. Copper gives an identical reaction and cobalt gives a red color. The conditions employed in making this test are essentially the same as those used in the quantitative determinations which are described in detail in the following sections.

Nickel is quantitatively precipitated as $(C_2H_5N_4O)_2Ni \cdot 2H_2O$ by the addition of dicyandiamidine sulfate to a solution of a nickel salt which has been made

alkaline with sodium or potassium hydroxide. Precipitation is quantitative and can be used for the gravimetric determination of nickel.^{5,11-15,30} This method is illustrated by the following procedure for the determination of nickel in steel.^{9,17,18}

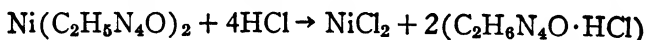
Procedure. Dissolve 0.5-2.0 g. of steel in aqua regia and evaporate to 10 ml. Filter from silica and other materials, and add 15 g. of Rochelle salt for each gram of steel used. Dissolve any precipitate which forms with a little ammonia. If much manganese is present, prevent oxidation by the use of a little hydrazine sulfate. Add ammonium hydroxide and 40 ml. of 20 per cent sodium hydroxide solution, and then add an excess of a cold 10 per cent solution of dicyandiamidine sulfate. If considerable nickel is present, filter as soon as the supernatant liquid is clear, but if only small quantities of nickel are present, allow the mixture to stand for some time before filtration. Filter through a Gooch crucible, wash with cold dilute ammonium hydroxide and dry at 120-130° C. The anhydrous compound contains 22.50 per cent of nickel. The factor for nickel is 0.2250.

Nicolardt and Gourmain¹⁹ have studied various methods which have been proposed for the determination of nickel and report that the dicyandiamidine method gives results comparable to those obtained with dimethylglyoxime, but that it requires greater care and offers more chance of error than with the latter reagent. Prettnner²⁰ claims that the dicyandiamidine method is superior to electrolytic procedures.

Grossmann²¹ has suggested a volumetric method for the determination of nickel based upon the titration of the nickel precipitate, formed with dicyandiamidine, with potassium cyanide solution, using silver iodide as the indicator. The precipitate is dissolved in dilute hydrochloric acid, a little ammonium chloride is added, and the mixture is made weakly alkaline with ammonium hydroxide before carrying out the titration.

Fluch²² and Dubsy and Hauer²³ have used dicyandiamidine for the precipitation of nickel as a preliminary to an acidimetric determination:

Procedure. Separate nickel from all metals except copper by precipitating with dicyandiamidine, and then wash the precipitate with 95 per cent alcohol to remove the excess potassium hydroxide and ammonia. Dissolve the precipitate in a measured volume of 0.2 N hydrochloric acid and titrate the excess with standard sodium hydroxide solution, using methyl red as the indicator. One atom of nickel in the precipitate corresponds to the neutralization of 4 moles of hydrochloric acid according to the following equation:



1 ml. of 0.1 N hydrochloric acid = 1.467 mg. of nickel.

Separation of nickel from iron. Dicyandiamidine has proved especially useful for the separation of nickel from such metals as cobalt, iron, zinc, magnesium, aluminum, chromium and manganese.

Grossmann and co-workers^{5,24-27} have found dicyandiamidine particularly useful for separating nickel from cobalt. The following procedure has been proposed by Grossmann and Schück.⁵

Procedure. Add a few drops of ammonium chloride solution to the solution containing the nickel and cobalt salts, then make alkaline with ammonium hydroxide and add a few ml. of hydrogen peroxide. Allow the mixture to stand for about a half hour until the cobalt is completely oxidized. The nickel is not affected. A slight excess of 10 per cent potassium hydroxide solution is then added, and the nickel is precipitated by the addition of an excess of 10 per cent solution of dicyandiamidine sulfate. Allow the mixture to stand overnight, then wash with water containing ammonia and dry at 120-130° C., or convert to nickel sulfate by heating with sulfuric acid and a few drops of fuming nitric acid.

Grossmann²⁵ has suggested the following improved procedure for separating nickel and cobalt. Cane sugar is used to prevent the precipitation of cobalt.

Procedure. Free the solution containing nickel and cobalt from excess acid and add ammonium hydroxide until the odor of ammonia is fairly strong. Add 10-20 ml. of 10 per cent cane sugar solution and an excess of 10 per cent dicyandiamidine sulfate solution. Add sodium hydroxide solution to precipitate the nickel. The smallest trace of nickel changes the color from blue to green and larger quantities cause formation of a yellowish precipitate. Cobalt, even in minute quantities, is indicated by the red to violet color of the liquid.

Separation of nickel and iron. Grossmann and co-workers²⁶⁻²⁸ recommend the following method for separating nickel from iron:

Procedure. To the solution of nickel and iron salts, which contains the least possible quantity of ammonium salts, add Rochelle salt in the proportion of 0.5-1.0 g. of the salt to each 0.2 g. of iron and nickel. Then add a large excess of ammonium hydroxide and add a concentrated solution of dicyandiamidine in such quantity that 1-2 g. of the reagent will be present for each 0.1 g. of nickel. Finally, add a sufficient quantity of cold 10 per cent potassium hydroxide to change the color of the solution from brownish-red to yellow, and allow the mixture to stand overnight in a cold place. Recover the nickel by filtration.

Other separations of nickel. Nickel may be separated from zinc by essentially the same procedure as that employed with cobalt (see above), but the treatment with hydrogen peroxide is not essential.^{5,27} Nickel may also be separated from chromium with the reagent in the presence of Rochelle salt unless the chromium is present as chromate. The chromium may also be converted to the complex acetate, which is not precipitated by alkalis in cold solutions.²⁰ For the separation of nickel from iron and aluminum an excess of tartrate is necessary to keep these metals in solution.^{26,27}

Detection of cobalt. Cobalt may be detected by means of the red-violet color which forms when dicyandiamidine is added to a strongly alkaline solution

of a cobalt salt containing cane sugar. The following procedure is recommended by Grossmann and Heilbron:⁷

Procedure. Free the solution from an excess of acid by evaporation, and then make strongly alkaline with ammonium hydroxide. Add 10-20 ml. of a 10 per cent solution of cane sugar, an excess of 10 per cent dicyandiamidine sulfate solution and a solution of sodium hydroxide. A violet-red color is produced with a fraction of a milligram of cobalt, and this may be observed in the presence of more than 100 times as much nickel, since the crystalline precipitate of nickel dicyandiamidine settles rapidly.

Determination of copper. Copper can be determined with dicyandiamidine in a manner similar to that used for nickel.¹⁶ The copper salt has an intense red color and is extremely resistant to the action of alkalies. The air-dried compound becomes rose-red on heating.

Procedure. To a solution containing copper, add an excess of a concentrated solution of dicyandiamidine sulfate in such quantity that about 2 g. of reagent is added for each 0.125 g. of copper. Make the mixture slightly alkaline with ammonium hydroxide, heat to boiling, and to the blue solution add sodium hydroxide until the color becomes reddish-violet. Avoid a large excess of sodium hydroxide. Discontinue the heating after addition of sodium hydroxide, since on long boiling in the presence of sodium hydroxide the precipitate of $\text{Cu}(\text{C}_2\text{H}_5\text{N}_4\text{O})_2 \cdot 2\text{H}_2\text{O}$ begins to decompose with the evolution of ammonia. Allow the mixture to cool, let stand, and filter the red crystalline precipitate through a Gooch crucible. Wash with cold water, dry at 120-140° C. to constant weight, and weigh as $\text{Cu}(\text{C}_2\text{H}_5\text{N}_4\text{O})_2$. The precipitate contains 23.923 per cent copper.

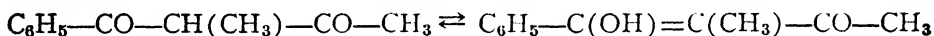
The copper compound is not completely insoluble in water, and so best results are obtained by using a concentrated solution of the copper salt and the least possible quantity of wash water. Precipitation of the copper compound is complete when the liquid above the precipitate is perfectly clear and colorless.

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2. L. Tschugaev, *Ber.* 40, 1975 (1907).
3. R. Weinland, *Einführung in die Chemie der Komplexverbindungen*, Leipzig.
4. H. Grisolle and M. Servigne, *Ann. chim. anal. chim. appl.* 12, 321-31 (1930); *C.A.* 25, 261 (1931).
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12. H. Grossmann and B. Schück, *Analyst.* 32, 273 (1907).
13. E. Cattelain, *J. pharm. chim.* [8] 2, 485, 525 (1925); *C.A.* 20, 1365 (1926).
14. I. Bellucci and A. Chiucini, *Gazz. chim. ital.* 49, 11, 187-216 (1919); *C.A.* 14, 908 (1920).

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17. H. Grossmann and B. Schück, *Analyst.* **35**, 247-8 (1910); *C.A.* **4**, 2916 (1910).
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22. P. Fluch, *Z. anal. Chem.* **69**, 232-43 (1926); *C.A.* **21**, 216 (1927).
23. J. V. Dubsky and E. Hauer, *Mikrochemie.* **12**, 321-6 (1933); *C.A.* **27**, 2109 (1933).
24. E. Ebler, *Z. anal. Chem.* **47**, 665-77 (1908); *C.A.* **3**, 294-5 (1909).
25. H. Grossmann, *Ind. chim.* **8**, 233 (1908); *C.A.* **2**, 3205 (1908).
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27. H. Grossmann and B. Schück, *Eng. Min. J.* **85**, 1044; *C.A.* **2**, 2200 (1908).
28. H. Grossmann and B. Schück, *Chem. Ztg.* **31**, 911-2 (1907); *C.A.* **2**, 644 (1908).
29. O. Schmitz-Duñont, *Metallwirtschaft.* **7**, 281-5 (1929).
30. E. Cattelain, *J. pharm. chim.* [8] **2**, 485-91, 525-35 (1925); *C.A.* **20**, 1365 (1926).

METHYLBENZOYLACETONE

$C_{11}H_{12}O_2$ Mol. Wt. 157.20 Biel. Ref. VII, 369.



Use: Detection of thallium.

Methylbenzoylacetone is a colorless liquid which boils at 150-152° C. at 30 mm.

Preparation: Warm 1 mole of benzoylacetone with 1 mole of sodium ethylate in methyl alcohol and dissolve as the sodium salt. Add 1.25 moles of methyl iodide and boil the mixture in a flask equipped with a reflux condenser until the mixture is no longer alkaline. This requires about 1-2 hours. The unreacted benzoylacetone is removed by extraction with the equivalent quantity of dilute sodium hydroxide solution. The pure compound distills at 150-152° C. at 30 mm. pressure.¹

Detection of thallium. When thallium carbonate is heated with a benzene solution of methylbenzoylacetone, a bright yellow crystalline compound is formed which corresponds in composition to the formula $C_{11}H_{11}O_2Tl$. Unlike other enolic compounds, the thallium compound of methylbenzoylacetone does not react with carbon disulfide.²

1. W. Dieckmann, *Ber.* **45**, 2686 (1912).

2. F. Feigl and E. Backer, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).

METHYL ETHYL KETONE

C_4H_8O Mol. Wt. 72.10 Beil. Ref. I, 666.



Use: Determination of cadmium, copper and mercury.

Methyl ethyl ketone is a colorless, inflammable liquid, having an acetone-like odor. It has a sp. gr. of 0.805 and boils at 79.6° C. It dissolves in 4 parts of water, but is miscible with alcohol, ether and benzene.

Preparation: Boil about 100 parts of methylacetoacetic ester with 25 parts of 20 per cent sulfuric acid with reflux. Distill and purify by converting to the bisulfite addition product. Decompose the addition product with sodium carbonate.¹

Determination of cadmium, copper and mercury. The complexes formed with Reinecke salt, thiourea and salts of cadmium, copper and mercury dissolve in organic solvents to form red solutions which are suitable for colorimetric comparison. Methyl ethyl ketone is recommended as the solvent.^{2,3}

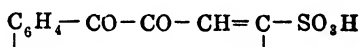
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2. C. Mahr, *Angew. Chem.* **53**, 257-8 (1940); *C.A.* **35**, 5406 (1941).
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β -NAPHTHOQUINONE-4-SULFONIC ACID

$C_{10}H_6O_5S$

Mol. Wt. 260.20

Beil. Ref. XI, 330.



Use: Determination of sulfate.

The sodium salt of β -naphthoquinone-4-sulfonic acid is obtained by crystallizing from 50 per cent alcohol. It is easily soluble in water but almost insoluble in alcohol.

Preparation: β -Naphthoquinone-4-sulfonic acid is prepared by the oxidation of 1-amino-2-naphthol-4-sulfonic acid (page 000) by oxidizing with 20 per cent nitric acid as follows: ¹ Mix gradually with stirring, aminonaphtholsulfonic acid with 1.5 times its weight of 20 per cent nitric acid. Dissolve the thick yellow paste of the ammonium salt of β -naphthoquinone-4-sulfonic acid in water and add a concentrated solution of potassium chloride. The potassium salt of the reagent separates as yellow needles.

Folin ² who has used this reagent in the analysis of amino acids, has described in detail a method for the preparation of β -naphthoquinone-4-sulfonic acid from β -naphthol.

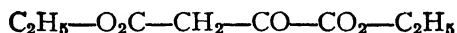
Determination of sulfate. β -Naphthoquinone-4-sulfonic acid reacts with benzidine to yield an intense stable color. This reaction has been used for the indirect determination of sulfate after precipitating as benzidine sulfate.³ Benzidine sulfate is made to react with β -naphthoquinone-4-sulfonic acid in the presence of a sodium borate-sodium hydroxide buffer, and acetone is added after the color reaction is completed to diminish the color of the reagent (see section on benzidine).

1. M. Boniger, *Ber.* **27**, 25 (1894).
2. O. Folin, *J. Biol. Chem.* **51**, 377-92 (1922).
3. V. T. Letonoff and J. G. Reinhold, *Am. J. Med. Sci.* **188**, 142 (1934).

OXALACETIC ACID ETHYL ESTER $C_8H_{12}O_5$

Mol. Wt. 188.18

Beil. Ref. III, 782.

**Use:** Detection of copper, iron and thallium.

This compound is a thick, colorless oil. It decomposes on standing. It has a sp. gr. of 1.159.

Preparation: Place 400 ml. of dry ether in a liter flask and add 11.5 g. of sodium wire, and then add 73 g. of ethyl oxalate. Fit the flask with a reflux condenser, and through this slowly add 55 g. of ethyl acetate. Heat the mixture on a water bath to about 30° C. for an hour and a half, or until all the sodium dissolves. Allow the mixture to stand overnight, and transfer the contents of the flask to a linen bag and squeeze out the solvent. Dry the residue on a porous plate in a vacuum desiccator. The solid is the sodium salt of the ester. To prepare the free ester, mix the sodium salt with 160 ml. of water, cover with ether, and carefully acidify with dilute sulfuric acid. Separate the ether, wash with dilute sodium carbonate solution, and dry over calcium chloride. Distill off the ether, and distill the residual ester *in vacuo* over a wire gauze. The boiling point at 20 mm. is 125-130° C.

Oxalacetic acid ethyl ester, like many other enolic compounds, reacts with solutions of thallium salts to form a yellow derivative. Unlike some other enols, however, the thallium derivative of this compound does not react with carbon disulfide.¹ On long standing with copper salts, the compound $Cu(C_8H_{11}O_5)_2$ is formed. An intense red color is formed when a dilute alcoholic solution of the reagent is added to ferric chloride.

1. F. Feigl and E. Backer, *Monatsh.* **49**, 385-400 (1928); *C.A.* **22**, 3659 (1928).

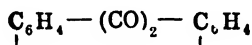
PHENANTHRENEQUINONE

Synonym: Phenanthraquinone

 $C_{14}H_8O_2$

Mol. Wt. 208.20

Beil. Ref. VII, 796.

**Use:** Detection of nitrate.

Phenanthrenequinone is an orange-red crystalline solid which melts at 203-205° C. It is insoluble in water, but is soluble in benzene, ether, glacial acetic acid and hot alcohol. It dissolves in concentrated sulfuric acid to give a dark green color.

Preparation: Dissolve 1 part of phenanthrene in 4-5 parts of warm acetic acid and mix with a hot solution containing 2.2 parts of chromic oxide in 5-6 parts of acetic acid. When the reaction is completed, boil the mixture for a short time and distill from the mixture the greater part of the acetic acid. To

the residue add water to precipitate phenanthrenequinone. To separate from anthraquinone, dissolve the precipitate in sodium bisulfite solution, precipitate the cold solution with sulfuric or hydrochloric acid and crystallize the precipitate from alcohol, benzene or acetic acid.¹

Detection of nitrate. Phenanthrenequinone dissolves in concentrated sulfuric acid to yield an intense dark green solution. A yellow color appears when potassium nitrate is added to this solution. The test is best carried out by adding a small crystal of the substance suspected of being a nitrate to a 0.02 per cent solution of phenanthrenequinone in sulfuric acid.²

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2. M. Eitel, *Z. anal. Chem.* **98**, 227-34 (1934); *C.A.* **29**, 71 (1935).

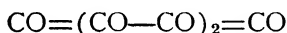
TRIQUINOYL

Synonym: Cyclohexanehexone

$C_6O_6 \cdot 8H_2O$

Mol. Wt. 312.19

Beil. Ref. VII, 907(500).



Use: Detection of barium, calcium and strontium.

Triquinoyl consists of colorless needles which melt at 95° C. with the evolution of carbon dioxide and water. It is almost insoluble in water, alcohol and ether, but is soluble in alkalies. It decomposes in aqueous solution to form rhodizonic acid.

Preparation: Triquinoyl is prepared by a method described by Schultz¹ and Nietzki and Benckiser.² For details, see preparation of rhodizonic acid.

Detection of barium. Barium hydroxide reacts with triquinoyl to give a rust-red compound having the formula $2C_6O_6 \cdot 3Ba(OH)_2 \cdot 6H_2O$.³ Gutzeit⁴ has used triquinoyl for the detection of barium. On warming triquinoyl with barium salts an orange-red color is obtained.

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2. R. Nietzki and Th. Benckiser, *Ber.* **18**, 1842 (1885).

3. F. Henle, *Ann.* **350**, 337 (1906).

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2,5-bis(2,4-dimethyl-N-pyrrolyl)-3,6-dibromohydroquinone, 195
chromotropic acid, 248
1,8-dihydroxynaphthalene-3,6-disulfonic acid, 248

Detection of Oxygen

acetone, 399
pyrocatechol, 159

Determination of Oxygen

anthraquinone- β -sulfonic acid, 412
2-chlorohydroquinone, 196
2,4-diaminophenol hydrochloride, 239
pyrocatechol, 159
pyrogallol, 171

Determination of Ozone

benzaldehyde, 373
butyraldehyde, 374
hexane, 59
2,2,4-trimethylpentane, 62

Detection of Palladium

4-amino-4'-hydroxydiphenyl sulfide, 194
carboxyphenyl-5-azo-8-hydroxyquinoline, 349
5-methyl-8-hydroxyquinoline, 341
phenyl-5-azo-8-hydroxyquinoline, 350
phloroglucinol, 155
5-(p-sulfophenylazo)-8-hydroxyquinoline, 353
5-(4-sulfo-1-naphthylazo)-8-hydroxyquinoline, 352
p-(4')-sulfo-8-tolyl-5-azo-8-hydroxyquinoline, 354
p-tolyl-5-azo-8-hydroxyquinoline, 355

Determination of Palladium

acetylene, 52
ethylene, 58

Determination of Periodate

formaldehyde, 382

Detection of Phosphorus

glycerol, 105
hydroquinone, 123

Determination of Phosphorus

1-amino-2-naphthol-4-sulfonic acid, 229

ascorbic acid, 81
n-butyl alcohol, 85
carbon tetrachloride, 65
ether, 365
gallic acid, 204
hydroquinone, 123
8-hydroxyquinoline, 311
isobutyl alcohol, 109
p-methylaminophenol, 241

Detection of Platinum

ether, 364
resorcinol, 177

Detection of Potassium

acetone, 398
1-amino-2-naphthol-6-sulfonic acid, 234
amyl alcohol, 75
ethyl alcohol, 94
7-nitro-8-hydroxyquinoline-5-sulfonic acid, 342

Determination of Potassium

acetone, 398
amyl alcohol, 76, 77
n-butyl alcohol, 82
dioxane, 358
ether, 366
ethyl alcohol, 88
n-hexyl alcohol, 106
isobutyl alcohol, 107
isopropyl alcohol, 111
methyl alcohol, 116
 β -naphthol, 144
phenol, 148
phenoldisulfonic acid, 258

Detection of Praseodymium

gallic acid, 203
pyrogallol, 167

Detection of Rare Earths

n-butyl alcohol, 85
gallic acid, 202
8-hydroxyquinoline, 311

Detection of Rhenium

chloroform, 68
cyclohexanol, 87
hydroquinone, 136
8-hydroxyquinoline, 314

Determination of Rhenium

cyclohexanol, 87
ether, 366

Detection of Rubidium

amyl alcohol, 75

Detection of Ruthenium

n-butyl alcohol, 85
ether, 364

Determination of Ruthenium

n-butyl alcohol, 85
8-hydroxyquinoline, 314

Detection of Selenium

acetone, 400

Determination of Selenium

acetone, 400
benzene, 55
ether, 366
hydroquinone, 136
toluene, 61

Detection of Silicon

2,4-diaminophenol hydrochloride, 240

Determination of Silicon

1-amino-2-naphthol-4-sulfonic acid, 232
glycerol, 105
8-hydroxyquinoline, 313
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amyl alcohol, 79
chloral, 374
chromotropic acid, 247
1,8-dihydroxynaphthalene-3,6-disulfonic acid, 247
formaldehyde, 380
gallic acid, 205
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hydroxyhydroquinone, 140
8-hydroxyquinoline-5-sulfonic acid, 335
p-methylaminophenol, 242
pyrogallol, 168
5,8-quinolinequinone-8-hydroxy-5-quinolyl-5-imide, 342
sozoiodol, 224
5-(p-sulfophenylazo)-8-hydroxy-quinoline, 353
p-tolyl-5-azo-8-hydroxyquinoline, 355

Determination of Silver

acetylene, 52
benzene, 55
chloral, 374
chloroform, 68
ether, 367, 368
ethyl alcohol, 97
formaldehyde, 380

gallic acid, 205
glycerol, 104
hydroquinone, 136
8-hydroxyquinoline-5-sulfonic acid, 335
isobutyl alcohol, 110
pyrogallol, 167
5,8-quinolinequinone-8-hydroxy-5-quinolyl-5-imide, 342

Detection of Sodium

amyl alcohol, 75
ethyl alcohol, 94

Determination of Sodium

amyl alcohol, 76, 77
n-butyl alcohol, 82
dioxane, 358
ether, 366
ethyl alcohol, 93
n-hexyl alcohol, 106
isobutyl alcohol, 107
isopropyl alcohol, 111
methyl alcohol, 116
resorcinol, 180

Detection of Strontium

amyl alcohol, 75
2,3-dihydroxyquinoxalin, 199
ethyl alcohol, 96
gallic acid, 205
7-iodo-8-hydroxyquinoline-5-sulfonic acid, 339
7-nitro-8-hydroxyquinoline-5-sulfonic acid, 342
pyrogallol, 168
rhodizonic acid, 219
triquinoyl, 425

Determination of Strontium

acetone, 393
amyl alcohol, 76
butyl cellosolve, 85
ether, 366
ethyl alcohol, 95, 96
isobutyl alcohol, 109
isopropyl alcohol, 111
methyl alcohol, 115
phenol, 151

Detection of Sulfate

rhodizonic acid, 222

Determination of Sulfate

acetone, 401
furfuraldehyde, 385
glycerol, 105
methyl cellosolve, 119
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Determination of Sulfate (Continued)

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Detection of Sulfite

formaldehyde, 381

Determination of Sulfur

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Detection of Tantalum

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pyrogallol, 165
resorcinol, 180

Determination of Tantalum

pyrogallol, 165

Detection of Thallium

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benzoylpyrroacemic acid ethyl ester, 416
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gallic acid, 205
methylbenzoylacetone, 422
oxalacetic acid ethyl ester, 424
sozoidol, 224

Determination of Thallium

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Detection of Thiocyanate

acetone, 396
formaldehyde, 381

Determination of Thiocyanate

acetone, 396
formaldehyde, 381

Determination of Thiosulfate

formaldehyde, 381

Detection of Thorium

gallic acid, 203
pyrogallol, 166
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Determination of Thorium

ether, 363
gallic acid, 203
8-hydroxyquinoline, 310

Detection of Tin

amyl alcohol, 79
phenol, 152

phloroglucinol, 155
resorcinol, 179
rhodizonic acid, 222

Determination of Tin

amyl alcohol, 79

Detection of Titanium

7-bromo-8-hydroxyquinoline-5-sulfonic acid, 323
chromotropic acid, 243
5,7-dibromo-8-hydroxyquinoline, 326
1,2-dihydroxybenzene-3,5-disulfonic acid, 251
1,8-dihydroxynaphthalene-3,6-disulfonic acid, 243
gallic acid, 203
hydroquinone, 134
5-methyl-8-hydroxyquinoline, 341
 α -naphthol, 141
 β -naphthol, 144
phenol, 152
pyrocatechol, 156
pyrogallol, 166, 168
resorcinol, 180
thymol, 186

Determination of Titanium

7-bromo-8-hydroxyquinoline-5-sulfonic acid, 323
chromotropic acid, 245
5,7-dibromo-8-hydroxyquinoline, 324
5,7-dichloro-8-hydroxyquinoline, 328
1,2-dihydroxybenzene-3,5-disulfonic acid, 251
1,8-dihydroxynaphthalene-3,6-disulfonic acid, 245
gallic acid, 203
8-hydroxyquinoline, 294
thymol, 186

Detection of Tungsten

hydroquinone, 134
8-hydroxyquinoline, 299, 302, 315
5-methyl-8-hydroxyquinoline, 341
 α -naphthol, 141
 β -naphthol, 144
pyrocatechol, 157

Determination of Tungsten

carbon tetrachloride, 65
hydroquinone, 134
8-hydroxyquinoline, 299

Detection of Uranium

gallic acid, 205
8-hydroxyquinoline, 302, 315
resorcinol, 180

Determination of Uranium

ether, 363
8-hydroxyquinoline, 302

Detection of Vanadium

4-amino-4'-hydroxydiphenyl sulfide, 194
p-aminophenol, 237
5,7-dibromo-8-hydroxyquinoline, 326
gallic acid, 204
hydroxyhydroquinone, 140
8-hydroxyquinoline, 298, 302, 315
8-hydroxyquinoline-5-sulfonic acid, 334
 α -naphthol, 141
phenol, 152
phloroglucinol, 155
pyrocatechol, 157, 158
pyrogallol, 167, 168
5-(p-sulfophenylazo)-8-hydroxyquinoline, 353

Determination of Vanadium

amyl alcohol, 78
carbon tetrachloride, 65
glycerol, 104
8-hydroxyquinoline, 297
8-hydroxyquinoline-5-sulfonic acid, 334
mannitol, 114
pyrocatechol, 158

Detection of Water

phenol, 152

Determination of Water

bicyclohexyl, 56
heptane, 59
toluene, 61
xylene, 62

Detection of Yttrium

gallic acid, 203

Detection of Zinc

acetylacetone, 407
alloxan, 192
benzoin, 413
chloroform, 67
ether, 364, 366
8-hydroxyquinoline, 284, 314, 315
7-iodo-8-hydroxyquinoline-5-sulfonic acid, 339
7-nitro-8-hydroxyquinoline-5-sulfonic acid, 342
phenyl-5-azo-8-hydroxyquinoline, 350
resorcinol, 177

Determination of Zinc

acrolein, 372
chloroform, 67
ether, 364
4-hydroxybenzothiazole, 209
8-hydroxyquinaldine, 331
8-hydroxyquinoline, 281
8-hydroxyquinoline-7-sulfonic acid, 335
8-hydroxyquinoline-5-sulfonic acid, 334
resorcinol, 178

Detection of Zirconium

acetylacetone, 407
8-hydroxyquinoline, 315
pyrogallolaldehyde, 387

Determination of Zirconium

chloroform, 68
5,7-dibromo-8-hydroxyquinoline, 327
8-hydroxyquinoline, 295

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